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

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

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

Answers:

1. (a) $C_9H_{18} + \frac{27}{2}O_2 \rightarrow 9\,CO_2 + 9\,H_2O$; $4\,FeS_2 + 11\,O_2 \rightarrow 2Fe_2O_3 + 8\,SO_2$
2. 3.08
3. 323
4. No
5. (a) 1,
   (b) 1,
   (c) The same,
   (d) The extent of reaction depends on the reaction equation as a whole and not on one species in the equation.
6. $CaCO_3$: 43.4%, CaO: 56.4%; (b) 0.308
7. (a) H_2SO_4
   (b) 79.2%;
   (c) 0.89
8. (a) C_2H_6 (the hydrogen is from reaction No.2, not the feed);
   (b) None;
   (c) Fraction conversion = 0.184;
   (d) 0.45;
   (e) 1.22
   (f) Based on reactant in the feed: 0.45, based on reactant consumed: 0.84, based on theory: 0.50;
   (g) Reaction (a) is 33 mol reacting and reaction (b) is 13.5 mol reacting, both based on 100 mol product.

2.5 Material Balances for Processes Involving Reaction

Species Material Balances

Processes Involving a Single Reaction

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

$$\left\{\begin{matrix}\text{moles of } i\\ \text{at } t_2\\ \text{in the system}\end{matrix}\right\} - \left\{\begin{matrix}\text{moles of } i\\ \text{at } t_1\\ \text{in the system}\end{matrix}\right\} = \left\{\begin{matrix}\text{moles of } i\\ \text{entering}\\ \text{the system}\end{matrix}\right\} - \left\{\begin{matrix}\text{moles of } i\\ \text{leaving}\\ \text{the system}\end{matrix}\right\} + \left\{\begin{matrix}\text{moles of } i\\ \text{generated}\\ \text{by reaction}\end{matrix}\right\} - \left\{\begin{matrix}\text{moles of } i\\ \text{consumed}\\ \text{by reaction}\end{matrix}\right\}$$

Note that we have written Equation (1) in **moles** rather than **mass** because the **generation** and **consumption** terms are more conveniently represented in **moles**.

For example : Figure 10.1 presents the process as an open, steady-state system operating for 1 min so that the accumulation terms are zero. The data in Figure 10.1 are in g mol.

Using Equation 10.1 you can calculate via a value in g mol for the **generation** or **consumption**, as the case may be, for each of the three species involved in the reaction:

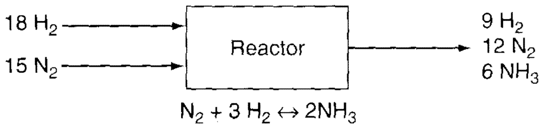


Figure 10.1. A reactor to produce NH_3.

NH_3 (generation): 6 – 0 = 6 gmol

H_2 (consumption): 9 – 18 = - 9 gmol

N_2 (consumption): 12 – 15 = - 3 gmol

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

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

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

$$\nu_{NH_3} = 2$$

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

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

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

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

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

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

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

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

The term <u>$\nu_i \xi$</u> corresponds to the moles of i **<u>generated or consumed</u>**.

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

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

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

Example 24

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

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

Solution

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

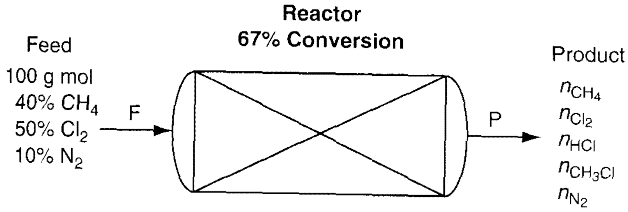


Figure E10.1

Basis 100 g mol feed

Limiting reactant:

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

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

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

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

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

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

$$n_{CH_4}^{out} = 40 - 1(26.8) = 13.2$$
$$n_{Cl_2}^{out} = 50 - 1(26.8) = 23.2$$
$$n_{CH_3Cl}^{out} = 0 + 1(26.8) = 26.8$$
$$n_{HCl}^{out} = 0 + 1(26.8) = 26.8$$
$$n_{N_2}^{out} = 10 - 0(26.8) = \underline{10.0}$$
$$100.0 = P$$

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

Example 25

A proposed process to remove H_2S is by reaction with SO_2: $2\,H_2S(g) + SO_2(g) \rightarrow 3S(s) + 2H_2O(g)$

In a test of the process, a gas stream containing 20% H_2S and 80% CH_4 were combined with a stream of pure SO_2. The process produced 5000 lb of S(s), and in the product gas the ratio of SO_2 to H_2S was equal to 3, and the ratio of H_2O to

H_2S was 10. You are asked to determine the fractional conversion of the limiting reactant, and the feed rates of the H_2S and SO_2 streams.

Solution

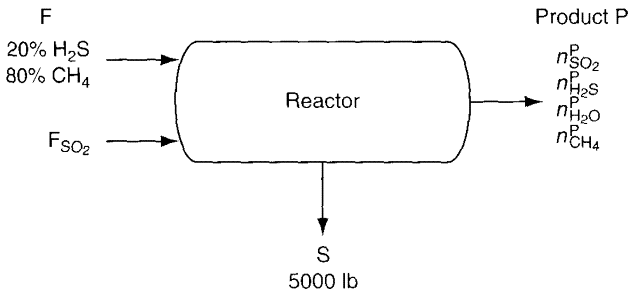


Figure E10.2

Basis is 5000 lb S (156.3 lb mol S)

Basis: S = 5000 lb (156.3 lb mol)

Specifications: 4 (3 independent) $x^F_{H_2S} = 0.20$ or $x^F_{CH_4} = 0.80$, $(n^P_{SO_2}/n^P_{H_2S}) = 3$, $(n^P_{H_2O}/n^P_{H_2S}) = 10$

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

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

$$H_2S\text{:} \quad n^P_{H_2S} = 0.20F - 2\,\xi \tag{b}$$

$$SO_2\text{:} \quad n^P_{SO_2} = F_{SO_2} - 1\,\xi \tag{c}$$

$$H_2O\text{:} \quad n^P_{H_2O} = 0 + 2\,\xi \tag{d}$$

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

The remaining specifications are

$$n^P_{SO_2} = 3n^P_{H_2S} \tag{f}$$

$$n^P_{H_2O} = 10n^P_{H_2S} \tag{g}$$

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

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

Then Equation (d) gives

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

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

Next, Equation (g) gives

And Equation (f) gives

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

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

F = 573 lb mol $\quad F_{SO_2} = 83.3$ lb mol $\quad n^F_{CH_4} = 458$ lb mol

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

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

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

Processes Involving Multiple Reactions

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

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

Where:

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

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

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

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

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

Where S is the number of species in the system.

Example 26

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

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

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

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

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

Solution

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

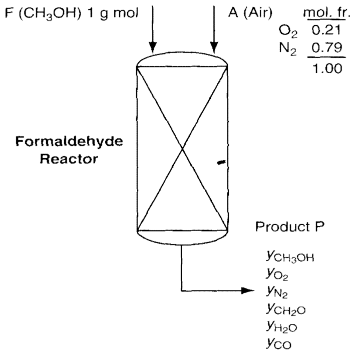


Figure E10.3

Basis: l gmol F

The **limiting** reactant is CH_3OH.

Use the fraction conversion, Equation 10.3: $\xi_1 = \frac{-0.90}{-1}(1) = 0.9$ g moles

The yield is related to ξ_i as follows

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

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

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

ξ_2 = 0.1 5 g moles reacting

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

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

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

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

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

Calculate P using Equation 10.5:

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

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

$$= 5.76 + [(-1) + (-\tfrac{1}{2}) + (1) + 0 + (1) + 0]\,0.9$$

$$+ [0 + (-\tfrac{1}{2}) + (-1) + 0 + (1) + (1)]\,0.15 = 6.28 \text{ g mol}$$

The material balances:

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

$$n_{O_2}^{out} = y_{O_2}(6.28) = 1.0 - (\tfrac{1}{2})(0.9) - (\tfrac{1}{2})(0.15) = 0.475$$

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

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

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

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

The six equations can be solved for the y_i :

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

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

Example 27

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

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

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

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

Solution

An unsteady-state process in a closed system

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

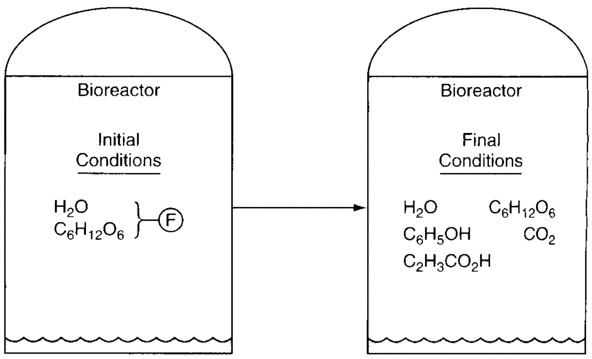


Figure E10.4

Basis: 4000 kg F

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

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

Specifications: 4 (3 independent)

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

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

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

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

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

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

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

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

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

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

$\xi_1 = 1.364$ kg moles reacting $\xi_2 = 0.801$ kg moles reacting

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

Note: The total mass of **3977 kg** is close enough to **4000 kg** of feed to validate the results of the calculations.

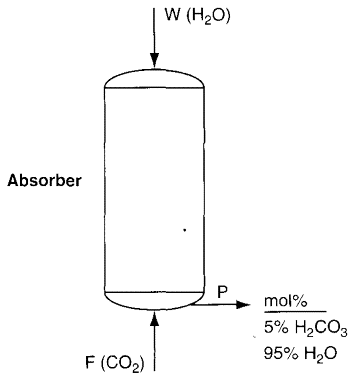
Element Material Balances

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

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

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

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



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

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

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

Figure 10.2 Schematic of the CO_2 absorber.

<u>Example 28</u>

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

Solution

1. <u>Example 24</u>

The element material balances are:

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

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

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

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

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

2. <u>Example 25</u>

The element balances are:

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

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

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

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

The solution of the problem will not change.

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

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

Example 29

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

Solution

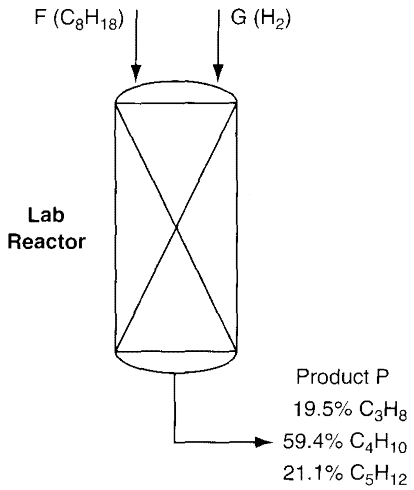


Figure E10.6

Basis: P= 100 g mol

Element balances: 2 H, C

The element balances:

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

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

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

The ratio

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

Material Balances Involving Combustion

- ⌘ **Combustion** is the reaction of a substance with **oxygen** with the associated release of energy and generation of product gases such as H_2O, CO_2, CO, and SO_2.
- ⌘ Most **combustion processes** use **air** as the source of **oxygen**. For our purposes you can assume that air contains **79% N_2** and **21% O_2**.

Special terms:

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