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

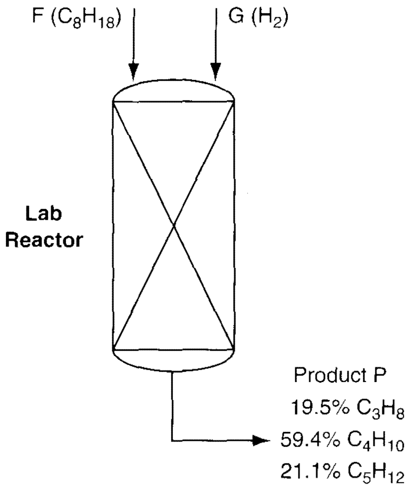

Figure E10.6

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).

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

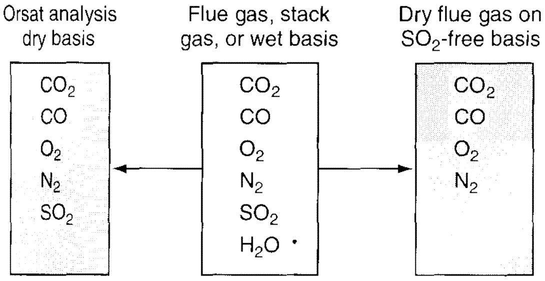

Figure 10.4 Comparison of a gas analysis on different bases.

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

The **percent excess air** is identical to the percent **excess** $\mathbf{O_2}$:

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

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

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

Or

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

Example 30

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

Solution

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

Basis: 20 kg of $\mathbf{C_3H_8}$

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

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

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

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

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

Note:

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

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

Solution

First, you can ignore the **information** about the **CO** and the **unburned ethane** because the basis of the calculation of **excess air is complete combustion**. Specifically C goes to CO_2; S to SO_2, H_2 to H_2O, CO goes to CO_2 and so on.

Second, the oxygen in the fuel cannot be ignored. Based on the reaction

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

Basis: 100 moles of gas

- 80 moles of C_2H_6 require 3.5(80) = 280 moles of O_2 for complete combustion.
- The gas contains 20 moles of O_2, so that only 280 – 20 = 260 moles of O_2 are needed in the entering air for complete combustion.
- Thus, 260 moles of O_2 are the required O_2 and the calculation of the 200% excess O_2 (air) is based on 260, not 280, moles of O_2:

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

Example 31

Figure E10.8 is a sketch of a fuel cell in which a continuous flow of methane (CH_4) and air (O_2 plus N_2) produce electricity plus CO_2 and H_2O. Special membranes and catalysts are needed to promote the reaction of CH_4. Based on the data given in Figure E10.8, you are asked to calculate the composition of the products in P.

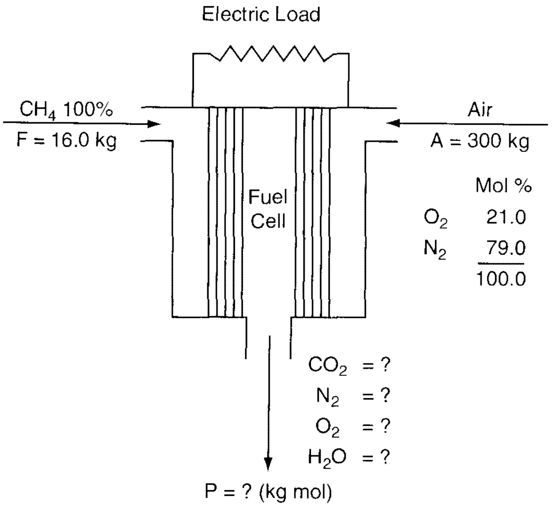

Figure E10.8

Solution

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

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

$$\frac{16.0 \text{ kg } CH_4}{} \left| \frac{1 \text{ kg mol } CH_4}{16.0 \text{ kg } CH_4} \right. = 1.00 \text{ kg mol } CH_4 \text{ in}$$

$$\frac{10.35 \text{ kg mol A}}{} \left| \frac{0.21 \text{ kg mol } O_2}{1 \text{ kg mol A}} \right. = 2.17 \text{ kg mol } O_2 \text{ in}$$

$$\frac{10.35 \text{ kg mol A}}{} \left| \frac{0.79 \text{ kg mol } N_2}{1 \text{ kg mol A}} \right. = 8.18 \text{ kg mol } N_2 \text{ in}$$

Basis: 16.0 kg CH_4 entering = 1 kg mol CH_4

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

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

The element material balances are (in moles):

$$\begin{array}{lll}
 & \text{Out} & & \text{In} \\
\text{C:} & n^P_{CO_2}(1) & = & 1(1) \\
\text{H:} & n^P_{H_2O}(2) & = & 1(4) \\
\text{O:} & n^P_{CO_2}(2) + n^P_{O_2}(2) + n^P_{H_2O}(1) & = & 2.17(2) \\
\text{2N:} & n^P_{N_2} & = & 8.18
\end{array}$$

The species material balances are:

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

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

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

The mole percentage composition of P is

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

Problems

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

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

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

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

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

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

   SiH_4, Si_2H_4, Si_2H_6, H_2, Si

   How many independent element balances can you make for this system?

5. Methane burns with O_2 to produce a gaseous product that contains CH_4, O_2, CO_2, CO, H_2O, and H_2. How many independent element balances can you write for this system?
6. Solve the problems (1, 2 & 3) using element balances.
7. Pure carbon is burned in oxygen. The flue gas analysis is: CO_2 75 mol%, CO 14 mol% & O_2 11 mol%. What was the percent excess oxygen used?
8. Toluene, C_7H_8, is burned with 30% excess air. A bad burner cause 15% of the carbon to form soot (pure C) deposited on the walls of the furnace, what is the Orsat analysis of the gases leaving the furnace?
9. A synthesis gas analyzing CO_2: 6.4%, O_2: 0.2%, CO: 40.0% and H_2: 50.8% (the balance is N_2) is burned with excess dry air. The problem is to determine the composition of the flue gas. How many degrees of freedom exist in this problem, that is, how many additional variables must be specified?
10. A coal analyzing 65.4% C, 5.3% H, 0.6% S, 1.1% N, 18.5% O, and 9.1% ash is burned so that all combustible is burnt out of the ash. The flue gas analyzes 13.00% CO_2, 0.76% CO, 6.17% O_2, 0.87% H_2, and 79.20% N_2. All of the sulfur burns to SO_2, which is included in the CO_2 in the gas analysis (i.e., CO_2 + SO_2 = 13%). Calculate:
    a. Pounds of coal fired per 100 lb mol of dry flue gas as analyzed;
    b. Ratio of moles of total combustion gases to moles of dry air supplied;
    c. Total moles of water vapor in the stack gas per 100 lb of coal if the entering air is dry;
    d. Percent excess air.
11. A hydrocarbon fuel is burnt with excess air. The Orsat analysis of the flue gas shows 10.2% CO_2, 1.0% CO, 8.4% O_2, and 80.4% N_2. What is the atomic ratio of H to C in the fuel?

<u>Answers:</u>

1. 186 kg
2. 887 lb
3. (a) C_6H_{12} = 139 mol/hr; (b) H_2O = 453 mol/hr; (c) CO = 347 mol/hr; (d) H_2 = 640 mol/hr; (e) C_6H_{14} = 53.3 mol/hr.
4. Two
5. Three
6. See the answers to the problems (1, 2 &3).
7. 4.5%
8. 9.1% CO_2, 8.9% O_2, 82% N_2
9. 1
10. (a) 252; (b)1.063; (c) 2.31; (d) 33.8%
11. 0.81

2.6 Material Balance Problems Involving Multiple Units

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