جامعة بابل – كلية هندسة المواد –قسم هندسة البوليمرات والصناعات البتروكيمياوية

مبادئ الهندسة الكيمياوية

Principles of Chemical Engineering

المرحلة الثانية

“The Chemical Equation and Stoichometry”

The chemical equation and Stoichometry

The objectives from studying this section are:

1. Write and balance chemical reaction equations.
2. Know the products of common reactions given the reactants.
3. Calculate the stoichiometric quantities of reactants and products given the chemical equation.
4. Define excess reactant, limiting reactant, conversion, degree of completion, and yield in a reaction.
5. Identify the limiting and excess reactants and calculate the percent excess reactant(s), the percent conversion, the percent completion, and yield for a chemical reaction with the reactants being in nonstoichiometric proportions.
6. Calculate the amount of products for incomplete reactions.

Example: Combustion of heptanes as shown below,

$$C_7H_{16} + 11\ O_2 \longrightarrow 7\ CO_2 + 8\ H_2O \tag{1.27}$$

First, make sure that the equation is balanced. Then you can see 1 mole (not lb_m or kg) of heptane will react with 11 moles of oxygen to give 7 moles of carbon dioxide plus 8 moles of water. These may be lb mol, g mol, or any other type of mole, as shown below.

$$C_7H_{16} + 11\ O_2 \longrightarrow 7\ CO_2 + 8\ H_2O$$

heptane	reacts with	oxygen	to give	carbon dioxide	and	water

Quantitative information

1 molecule of heptane	reacts with	11 molecules of oxygen	to give	7 molecules of carbon dioxide	and	8 molecules of water
6.023×10^{23} molecules of C_7H_{16}	+	$11(6.023 \times 10^{23})$ molecules of O_2	$\longrightarrow$	$7(6.023 \times 10^{23})$ molecules of CO_2	+	$8(6.023 \times 10^{23})$ molecules of H_2O

$$C_7H_{16} + 11\ O_2 \longrightarrow 7\ CO_2 + 8\ H_2O$$

1 g mole of C_7H_{16}	+	11 g moles of O_2	$\longrightarrow$	7 g moles of CO_2	+	8 g moles of H_2O
1 kg mole of C_7H_{16}	+	11 kg moles of O_2	$\longrightarrow$	7 kg moles of CO_2	+	8 kg moles of H_2O
1 lb mole of C_7H_{16}	+	11 lb moles of O_2	$\longrightarrow$	7 lb moles of CO_2	+	8 lb moles of H_2O
1 ton mole of C_7H_{16}	+	11 ton moles of O_2	$\longrightarrow$	7 ton moles of CO_2	+	8 ton moles of H_2O

$$\underbrace{\underbrace{1(100)\text{ g of } C_7H_{16}}_{100\text{ g}} + \underbrace{11(32)\text{ g of } O_2}_{352\text{ g}}}_{452\text{ g}} = \underbrace{\underbrace{7(44)\text{ g of } CO_2}_{308\text{ g}} + \underbrace{8(18)\text{ g of } H_2O}_{144\text{ g}}}_{452\text{ g}}$$

$$452\text{ kg} = 452\text{ kg}$$

$$452\text{ ton} = 452\text{ ton}$$

$$452\text{ lb} = 452\text{ lb}$$

Figure 1.15 Application of the chemical equation.

One mole of CO_2 is formed each 1/7 mole of C_7H_{16}. Also, 1 mole of H_2O is formed with each 7/8 mole of CO_2. Thus the equation tell us in terms of moles (not mass) the ratios among reactants and products. The coefficients of the compounds in the equation are known as stoichiometric coefficients:
1 for C_7H_{16} , 11 for O_2 and so on.

Stoichiometry (stoi-ki-om-e-tri)[10] deals with the combining weights of elements and compounds. The ratios obtained from the numerical coefficients in the chemical equation are the **stoichiometric ratios** that permit you to calculate the moles of one substance as related to the moles of another substance in the chemical equation. If the basis selected is to be mass (lb_m, kg) rather than moles, you should use the following method in solving problems involving the use of chemical equations: (1) Use the molecular weight to calculate the number of moles of the substance equivalent to the basis; (2) change this number of moles into the corresponding number of moles of the desired product or reactant by multiplying by the proper stoichiometric ratio, as determined by the chemical equation; and (3) then change the moles of product or reactant to a mass. These steps are indicated in Fig. 1.16 for the reaction in Eq. (1.27). You can combine these steps in a single dimensional equation, as shown in the examples below, for case of calculations.

Basis : 10.0 kg C_7H_{16}

Component	Mol. wt
C_7H_{16}	100.1
O_2	32.0
CO_2	44.0
H_2O	18.0

$$\begin{array}{ccccccc} \text{1 kg mole} & & & & \text{7 kg mole} & & \\ C_7H_{16} & + & 11O_2 & \longrightarrow & 7CO_2 & + & 8H_2O \end{array}$$

$$\frac{10.0 \text{ kg } C_7H_{16}}{\dfrac{100.1 \text{ kg } C_7H_{16}}{\text{kg mole } C_7H_{16}}} = 0.100 \text{ kg mole } C_7H_{16} \longrightarrow \frac{0.700 \text{ kg mole } CO_2}{\dfrac{1 \text{ kg mole } CO_2}{44.0 \ \ CO_2}} = 30.8 \text{ kg } CO_2$$

10.0 kg C_7H_{16} yields 30.8 kg CO_2

Figure 1.16 Stoichiometry.

EXAMPLE 1.27 Use of the Chemical Equation

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 Fig. E1.27. How many kilograms of heptane must be burned per hour?

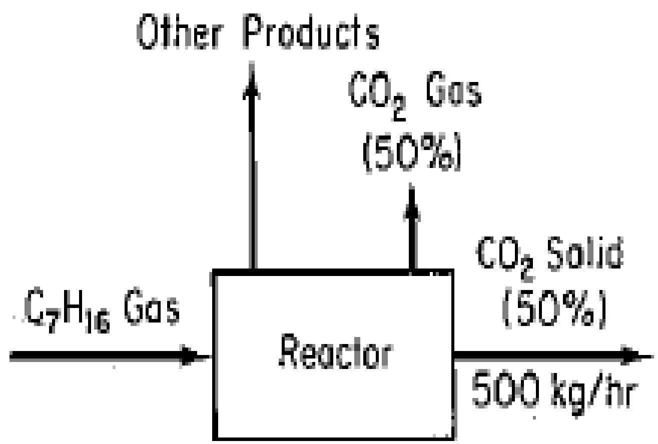

Figure E1.27

Solution

Basis: 500 kg of dry ice (or 1 hr)

Mol. wt. heptane = 100.1. Chemical equation as in Fig. 1.15.

$$\frac{500 \text{ kg dry ice}}{} \left| \frac{1 \text{ kg } CO_2}{0.5 \text{ kg dry ice}} \right| \frac{1 \text{ kg mol } CO_2}{44 \text{ kg } CO_2} \left| \frac{1 \text{ kg mol } C_7H_{16}}{7 \text{ kg mol } CO_2} \right| \frac{100.1 \text{ kg } C_7H_{16}}{1 \text{ kg mol } C_7H_{16}} = 325 \text{ kg } C_7H_{16}$$

Since the basis of 500 kg of dry ice is identical to 1 hr, 325 kg of C_7H_{16} must be burned per hour. Note that kilograms are first converted to moles, then the chemical equation is applied, and finally moles are converted to kilograms again for the final answer.

EXAMPLE 1.28 Stoichiometry

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:

$$2Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4$$

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? See Fig. E1.28.

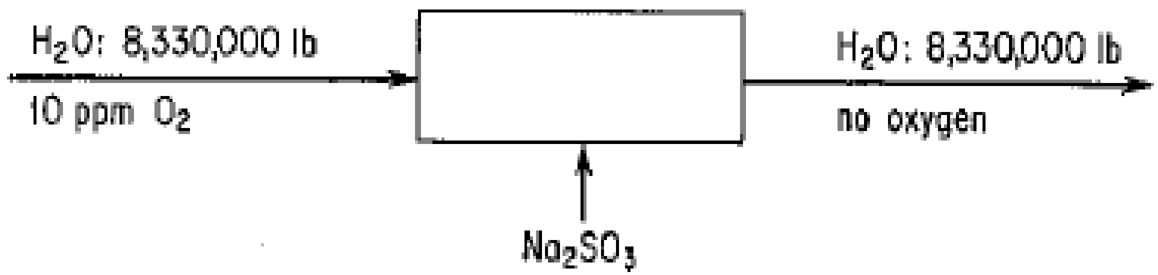

Figure E1.28

Solution

Additional data: mol. wt. of Na_2SO_3 is 126. Chemical equation: $2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$.

Basis: 8,330,000 lb of H_2O with 10 ppm O_2 or 83.3 lb of O_2

$$\frac{8{,}330{,}000 \text{ lb } H_2O}{} \left| \frac{10 \text{ lb } O_2}{\underbrace{(1{,}000{,}000 - 10 \text{ lb } O_2)\text{lb } H_2O}_{\textbf{effectively same as 1,000,000}}} \right. = 83.3 \text{ lb } O_2$$

$$\frac{8{,}330{,}000 \text{ lb } H_2O}{} \left| \frac{10 \text{ lb } O_2}{10^6 \text{ lb } H_2O} \right| \frac{1 \text{ lb mol } O_2}{32 \text{ lb } O_2} \left| \frac{2 \text{ lb mol } Na_2SO_3}{1 \text{ lb mol } O_2} \right.$$

$$\left| \frac{126 \text{ lb } Na_2SO_3}{1 \text{ lb mol } Na_2SO_3} \right| \frac{1.35}{1} = 886 \text{ lb } Na_2SO_3$$

EXAMPLE 1.29 Stoichiometry

A limestone analyzes

$CaCO_3$	92.89%
$MgCO_3$	5.41%
Insoluble	1.70%

(a) How many pounds of calcium oxide can be made from 5 tons 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

Read the problem carefully to fix in mind exactly what is required. Lime will include all the impurities present in the limestone which remain after the CO_2 has been driven off. Next, draw a picture of what is going on in this process. See Fig. E1.29.

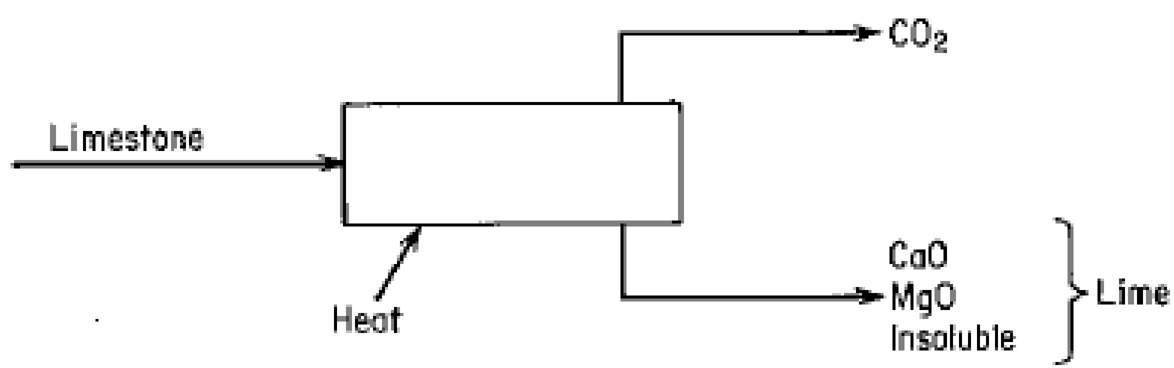

Figure E1.29

To complete the preliminary analysis you need the following chemical equations:

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$MgCO_3 \longrightarrow MgO + CO_2$$

Additional data:

	$CaCO_3$	$MgCO_3$	CaO	MgO	CO_2
Mol. wt.:	100.1	84.32	56.08	40.32	44

Basis: 100 lb of limestone

This basis was selected because pounds = percent.

Component	lb = percent	lb mol	Lime	lb	CO_2 (lb)
$CaCO_3$	92.89	0.9280	CaO	52.2	40.8
$MgCO_3$	5.41	0.0642	MgO	2.59	2.82
Insoluble	1.70		Insoluble	1.70	
Total	100.00	0.9920	Total	56.4	43.6

Note that the total pounds of products equal the 100 lb of entering limestone. Now to calculate the quantities originally asked for:

(a) $$\text{CaO produced} = \frac{52.2 \text{ lb CaO}}{100 \text{ lb stone}} \left| \frac{2000 \text{ lb}}{1 \text{ ton}} \right| \frac{5 \text{ ton}}{} = 5220 \text{ lb CaO}$$

(b) $$CO_2 \text{ recovered} = \frac{43.6 \text{ lb } CO_2}{100 \text{ lb stone}} = 0.436 \text{ lb}$$

or

(c) $$\text{Limestone required} = \frac{100 \text{ lb stone}}{56.4 \text{ lb lime}} \left| \frac{2000 \text{ lb}}{1 \text{ ton}} \right. = 3546 \text{ lb stone}$$

(a) **Limiting reactant is the reactant that is present in the smallest stoichiometric amount.** In other words, if two or more reactants are mixed and if the reaction were to proceed according to the chemical equation to completion, **whether it does or not,** the reactant that would first disappear is termed the limiting reactant. For example, using Eq. (1.27), if 1 g mol of C_7H_{16} and 12 g mol of O_2 are mixed, C_7H_{16} would be the limiting reactant even if the reaction does not take place.

(b) **Excess reactant is a reactant present in excess of the limiting reactant.** The **percent excess** of a reactant is based on the amount of any excess reactant above the amount required to react with the limiting reactant according to the chemical equation, or

$$\% \text{ excess} = \frac{\text{moles in excess}}{\text{moles required to react with limiting reactant}}(100)$$

where the moles in excess frequently can be calculated as the total available moles of a reactant less the moles required to react with the limiting reactant. A common term, **excess air,** is used in combustion reactions; it means the amount of air available to react that is in excess of the air theoretically required to *completely* burn the combustible material. The *required* amount of a reactant is established by the limiting reactant and is for all other reactants the corresponding stoichiometric amount. **Even if only part of the limiting reactant actually reacts, the required and excess quantities are based on the entire amount of the limiting reactant as if it had reacted completely.**

(c) **Conversion is the fraction of the feed or some material in the feed that is converted into products.** Thus, percent conversion is

$$100 \frac{\text{moles of feed (or a compound in the feed) that react}}{\text{moles of feed (or a compound in the feed) introduced}}$$

What the basis in the feed is for the calculations and into what products the basis is being converted must be clearly specified or endless confusion results. Conversion is related to the **degree of completion** of a reaction, which is usually the percentage or fraction of the limiting reactant converted into products.

(d) **Selectivity is the ratio of the moles of a particular (usually the desired) product produced to the moles of another (usually undesired) product produced** in a set of reactions.

(e) **Yield,** for a single reactant and product, is the weight (mass) or moles of final product divided by the weight (mass) or moles of initial reactant (P lb of product A per R lb of reactant B) either fed or consumed. If more than one product and more than one reactant are involved, the reactant upon which the yield is to be based must be clearly stated. Suppose that we have a reaction sequence as follows:

$$\begin{tikzcd} A \arrow[r] \arrow[dr] & B \arrow[r] & C \\ & C & \end{tikzcd}$$

With B the desired product and C the undesired one. The yield of B is the moles (or mass) of B produced divided by the moles (or mass) of A fed or consumed. The selectivity of B is the moles of B divided by the moles of C produced.

The terms "yield" and "selectivity" are terms that measure the degree to which a desired reaction proceeds relative to competing alternative (undesirable) reactions. As a designer of equipment you want to maximize production of the desired product and minimize production of the unwanted products. Do you want high or low selectivity? Yield?

EXAMPLE 1.30 Limiting Reactant and Incomplete Reaction

Antimony is obtained by heating pulverized stibnite (Sb_2S_3) with scrap iron and drawing off the molten antimony from the bottom of the reaction vessel:

$$Sb_2S_3 + 3Fe \longrightarrow 2Sb + 3FeS$$

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. Calculate:

(a) The limiting reactant
(b) The percentage of excess reactant
(c) The degree of completion (fraction)
(d) The percent conversion
(e) The yield

Solution

The molecular weights needed to solve the problem and the gram moles forming the basis are:

Component	kg	Mol. wt.	g mol
Sb_2S_3	0.600	339.7	1.77
Fe	0.250	55.85	4.48
Sb	0.200	121.8	1.64
FeS		87.91	

The process is illustrated in Fig. E1.30.

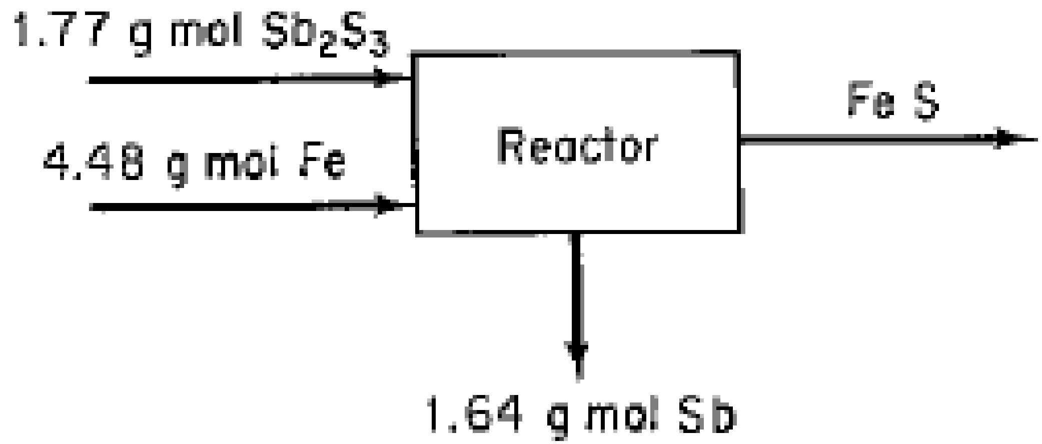

Figure E1.30

(a) To find the limiting reactant, we examine the chemical reaction equation and note that if 1.77 g mol of Sb_2S_3 reacts, it requires 3(1.77) = 5.31 g mol of Fe, whereas if 4.48 g mol of Fe reacts, it requires (4.48/3) = 1.49 g mol of Sb_2S_3 to be available. Thus Fe is present in the smallest stoichiometric amount and is the limiting reactant; Sb_2S_3 is the excess reactant.

(b) The percentage of excess reactant is

$$\% \text{ excess} = \frac{1.77 - 1.49}{1.49}(100) = 18.8\% \text{ excess } Sb_2S_3$$

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

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

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

$$\text{fractional degree of completion} = \frac{2.46}{4.48} = 0.55$$

(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.

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

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

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

$$\text{yield} = \frac{0.200 \text{ kg Sb}}{0.600 \text{ kg } Sb_2S_3} = \frac{1}{3}\frac{\text{kg Sb}}{\text{kg } Sb_2S_3} = \frac{0.33 \text{ kg Sb}}{1 \text{ kg } Sb_2S_3}$$

EXAMPLE 1.31 Limiting Reactant and Incomplete Reactions

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

$$Al_2O_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O$$

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

We will omit the figure for this problem. You need to look up or calculate the molecular weights of the compounds involved. The pound moles of substances forming the basis of the problem can be computed as follows:

$$\frac{1798 \text{ lb } Al_2(SO_4)_3}{} \left| \frac{1 \text{ lb mol } Al_2(SO_4)_3}{342.2 \text{ lb } Al_2(SO_4)_3} \right. = 5.25 \text{ lb mol}$$

$$\frac{1080 \text{ lb bauxite}}{} \left| \frac{0.554 \text{ lb } Al_2O_3}{1 \text{ lb bauxite}} \right| \frac{1 \text{ lb mol } Al_2O_3}{101.96 \text{ lb } Al_2O_3} = 5.87 \text{ lb mol}$$

$$\frac{2510 \text{ lb acid}}{} \left| \frac{0.777 \text{ lb } H_2SO_4}{1 \text{ lb acid}} \right| \frac{1 \text{ lb mol } H_2SO_4}{98.1 \text{ lb } H_2SO_4} = 19.88 \text{ lb mol}$$

(a) The excess reactant can be determined as follows:

	Ratio in feed	*Ratio in chemical equation*
	$\dfrac{H_2SO_4}{Al_2O_3} : \dfrac{19.88}{5.87} = 3.39$	$\dfrac{3}{1} = 3$

Hence H_2SO_4 is the excess reactant.

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

$$\frac{5.25 \text{ lb mol } Al_2(SO_4)_3 \;\Big|\; 3 \text{ lb mol } H_2SO_4}{\;\Big|\; 1 \text{ lb mol } Al_2(SO_4)_3} = 15.75 \text{ lb mol } H_2SO_4 \text{ was consumed}$$

$$\frac{15.75}{19.88}(100) = 79.2\%$$

(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:

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

EXAMPLE 1.32 The Meaning of Selectivity and Yield

Two well-known reactions take place in the dehydrogenation of ethane:

$$C_2H_6 \longrightarrow C_2H_4 + H_2 \tag{a}$$

$$C_2H_6 + H_2 \longrightarrow 2CH_4 \tag{b}$$

Given the following product distribution (in the gas-phase reaction of C_2H_6 in the presence of H_2) from the reaction of C_2H_6

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

what is (a) the selectivity of C_2H_4 relative to CH_4 and (b) the yield of C_2H_4 in kilogram moles of C_2H_4 per kilogram mole of C_2H_6?

Solution

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.

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

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

$$33.5 \text{ kg mol } C_2H_6$$

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

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

Questions

1. Write balanced reaction equations for the following reactions:
   (a) C_9H_{18} and oxygen to form carbon dioxide and water
   (b) FeS_2 and oxygen to form Fe_2O_3 and sulfur dioxide

Ans.

1. (a) $C_9H_{18} + \frac{27}{2}O_2 \longrightarrow 9CO_2 + 9H_2O$
   (b) $FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$

2. If 1 kg of benzene (C_6H_6) is oxidized with oxygen, how many kilograms of O_2 are needed to convert all the benzene to CO_2 and H_2O?

Ans. 3.08

3. The electrolytic manufacture of chlorine gas from a sodium chloride solution is carried out by the following reaction:

$$2NaCl + 2H_2O \longrightarrow 2NaOH + H_2 + Cl_2$$

How many kilograms of Cl_2 can one produce from 10 m^3 of a brine solution containing 5% by weight of sodium chloride? The specific gravity of the solution relative to water at 4°C is 1.07.

Ans. 323

5. In problem 3, suppose that 50.0 kg of NaCl reacts with 10.0 kg of H_2O.
   (a) What is the limiting reactant?
   (b) What is the excess reactant?
   (c) What components will the product solution contain if the reaction is 60% complete?

Ans.

(a) H_2O
(b) NaCl
(c) NaCl, H_2O, NaOH (assuming that the gas escapes)