Chapter 9

The Chemical Reaction Equation and Stoichiometry

9.1 Stoichiometry

- The stoichiometric coefficients in the chemical reaction equation
  $C_7H_{16}(\ell) + 11\ O_2(g) \rightarrow 7\ CO_2(g) + 8\ H_2O(g)$ Is (1 for C_7H_{16}, 11 for O_2 and so on).
- Another way to use the chemical reaction equation is to indicate that **1 mole of CO_2** is formed from each **(1/7) mole of C_7H_{16}**, and **1 mole of H_2O** is formed with each **(7/8) mole of CO_2**. The latter ratios indicate the use of **stoichiometric ratios** in determining the relative proportions of products and reactants.

For example how many kg of CO_2 will be produced as the product if 10 kg of C_7H_{16} react completely with the **stoichiometric quantity** of O_2? On the basis of 10 kg of C_7H_6

$$\frac{10\text{ kg } C_7H_{16}}{} \left| \frac{1\text{ kg mol } C_7H_{16}}{100.1\text{ kg } C_7H_{16}} \right| \frac{7\text{ kg mol } CO_2}{1\text{ kg mol } C_7H_{16}} \left| \frac{44.0\text{ kg } CO_2}{1\text{ kg mol } CO_2} \right. = 30.8\text{ kg } CO_2$$

Example 9.1

The primary energy source for cells is the aerobic catabolism (oxidation) of glucose ($C_6H_{12}O_6$, a sugar). The overall oxidation of glucose produces CO_2 and H_2O by the following reaction

$$C_6H_{12}O_6 + aO_2 \rightarrow b\,CO_2 + c\,H_2O$$

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

Solution

Basis: The given reaction

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

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

Gives a = 6. Therefore, the balanced equation is $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

Example 9.2

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 E9.2. How many kilograms of heptane must be burned per hour? (MW: CO_2 = 44 and C_7H_{16} = 100.1)

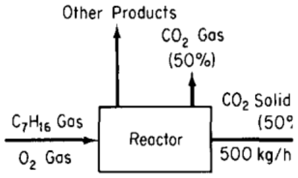


Figure E9.2

Solution

The chemical equation is $C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$

Basis: 500 kg of dry ice (equivalent to 1 hr)

The calculation of the amount of C_7H_{16} can be made in one sequence:

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

Example 9.3

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

By heating the limestone you recover oxides known as lime.

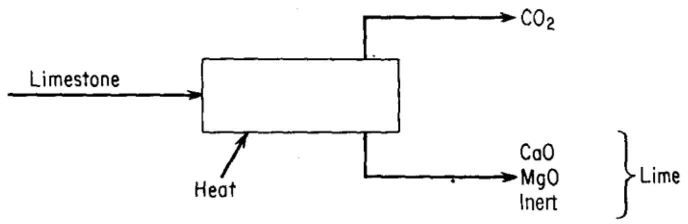
(a) How many pounds of calcium oxide can be made from 1 ton of this limestone?

(b) How many pounds of CO_2 can be recovered per pound of limestone?

(c) How many pounds of limestone are needed to make 1 ton of lime?

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

Solution



Chemical Equation:

$$CaCO_3 \rightarrow CaO + CO_2$$
$$MgCO_3 \rightarrow MgO + CO_2$$

Basis: 100 lb of limestone

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

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

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

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

The production of $\mathbf{CO_2}$ is:

0.9280 lb mol CaO is equivalent to **0.9280 lb mol $\mathbf{CO_2}$**

0.0642 lb mol MgO is equivalent to **0.0642 lb mol $\mathbf{CO_2}$**

Total lb mol CO_2 = 0.9280 + 0.0642 = **0.992 lb mol $\mathbf{CO_2}$**

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

Alternately, you could have calculated the **lb $\mathbf{CO_2}$** from a total balance: **100 - 56.33 = 44.67**.

Now, to calculate the quantities originally asked for:

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

(b) CO_2 recovered = $\frac{43.65 \text{ lb } CO_2}{100 \text{ lb limestone}} = 0.437 \text{ lb } CO_2\text{/lb limestone}$

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

9.2 Terminology for Applications of Stoichiometry

9.2.1 Extent of Reaction

The **extent of reaction**, ξ, is based on a particular stoichiometric equation, and denotes how much reaction occurs.

The extent of reaction is defined as follows: $$\xi = \frac{n_i - n_{io}}{v_i} \quad \ldots 9.1$$

Where:

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

n_{io} = moles of species *i* present in the system when the reaction starts

v_i = coefficient for species *i* in the particular chemical reaction equation (moles of species *i* produced or consumed per moles reacting)

ξ = extent of reaction (moles reacting)

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

Equation (9.1) can be rearranged to calculate the number of moles of component *i* from the value of the extent of reaction

$$n_i = n_{i0} + \xi v_i \qquad \dots 9.2$$

<u>Example 9.4</u>

Determine the extent of reaction for the following chemical reaction $N_2 + 3H_2 \rightarrow 2NH_3$ given the following analysis of feed and product:

	N_2	H_2	NH_3
Feed	100 g	50 g	5 g
Product			90 g

Also, determine the g and g mol of N_2 and H_2 in the product.

Solution

The extent of reaction can be calculated by applying Equation 9.1 based on NH_3:

$$n_i = \frac{90 \text{ g } NH_3}{} \left| \frac{1 \text{ g mol } NH_3}{17 \text{ g } NH_3} \right. = 5.294 \text{ g mol } NH_3$$

$$n_{i0} = \frac{5 \text{ g } NH_3}{} \left| \frac{1 \text{ g mole } NH_3}{17 \text{ g } NH_3} \right. = 0.294 \text{ g mol } NH_3$$

$$\xi = \frac{n_i - n_{i0}}{v_i} = \frac{(5.294 - 0.204)\text{g mol } NH_3}{2 \text{ g mol } NH_3/\text{moles reacting}} = 2.50 \text{ moles reacting}$$

Equation 9.2 can be used to determine the g mol of N_2 and H_2 in the products of the reaction

$$N_2: \quad n_{i0} = \frac{100 \text{ g } N_2}{} \left| \frac{1 \text{ g mol } N_2}{28 \text{ g } N_2} \right. = 3.57 \text{ g mol } N_2$$

$$n_{N_2} = 3.57 + (-1)(2.5) = 1.07 \text{ g mol } N_2$$

$$m_{N_2} = \frac{1.07 \text{ g mol } N_2}{} \left| \frac{28 \text{ g } N_2}{1 \text{ g mol } N_2} \right. = 30 \text{ g } N_2$$

$$H_2: \quad n_{i0} = \frac{50 \text{ g } H_2}{} \left| \frac{1 \text{ g mol } H_2}{2 \text{ g } H_2} \right. = 25 \text{ g mol } H_2$$

$$n_{H2} = 25 + (-3)(2.5) = 17.5 \text{ g mol } H_2$$

$$m_{H2} = \frac{17.5 \text{ g mol } H_2}{} \left| \frac{2\text{g } H_2}{1 \text{ g mol } H_2} \right. = 35 \text{ g } H_2$$

<u>Note</u>: If several independent reactions occur in the reactor, say *k* of them, ξ can be defined for each reaction, with v_{ki} being the stoichiometric coefficient of species *i* in the *k*th reaction, the total number of moles of species *i* is

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

Where R is the total number of independent reactions.

9.2.2 Limiting and Excess Reactants

- ❖ The **excess material** comes out together with, or perhaps separately from, the product, and sometimes can be used again.
- ❖ The **limiting reactant** is the species in a chemical reaction that would theoretically run out first (**would be completely consumed**) if the reaction were to proceed to completion according to the chemical equation—**even if the reaction does not proceed to completion!** All the other reactants are called **excess reactants**.

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

- ❖ **<u>For example</u>**, using the chemical reaction equation in **Example 9.2**,

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

If **1 g mol of C_7H_{16}** and **12 g mol of O_2** are mixed.

As a straightforward way of determining the **limiting reactant**, you can determine the **maximum extent of reaction**, ξ^{max}, for each reactant based on the **complete reaction** of the reactant. **The reactant with the smallest maximum extent of reaction is the limiting reactant**. For the example, for **1 g mol** of **C_7H_{16}** plus **12 g mole** of **O_2**, you calculate

$$\xi^{max}\,(\text{based on } O_2) = \frac{0 \text{ g mol } O_2 - 12 \text{ g mol } O_2}{-11 \text{ g mol } O_2/\text{moles reacting}} = 1.09 \text{ moles reacting}$$

$$\xi^{max}\,(\text{based on } C_7H_{16}) = \frac{0 \text{ g mol } C_7H_{16} - 1 \text{ g mol } C_7H_{16}}{-1 \text{ g mol } C_7H_{16}/\text{moles reacting}} = 1.00 \text{ moles reacting}$$

Therefore, **heptane** is the **limiting reactant** and **oxygen** is the **excess reactant**.

As an **alternate** to determining the **limiting reactant**,

$$\frac{O_2}{C_7H_{16}}: \quad \underline{\textit{Ratio in feed}}\ \ \frac{12}{1} = 12 \quad > \quad \underline{\textit{Ratio in chemical equation}}\ \ \frac{11}{1} = 11$$

❖ Consider the following reaction $A + 3B + 2C \rightarrow \text{Products}$

If the feed to the reactor contains **1.1 moles of A**, **3.2 moles of B**, and **2.4 moles of C**. The extents of reaction based on complete reaction of **A, B,** and **C** are

$$\xi^{max}\ (\text{based on A}) = \frac{-1.1 \text{ mol A}}{-1} = 1.1$$

$$\xi^{max}\ (\text{based on B}) = \frac{-3.2 \text{ mol B}}{-3} = 1.07$$

$$\xi^{max}\ (\text{based on C}) = \frac{-2.4 \text{ mol C}}{-2} = 1.2$$

As a result, **B** is identified as the **limiting reactant** in this example while **A** and **C** are the **excess reactants**.

As an **alternate** to determining the **limiting reactant** for same example:

We **choose A** as the **reference substance** and calculate

	Ratio in feed		*Ratio in chemical equation*
$\frac{B}{A}$:	$\frac{3.2}{1.1} = 2.91$	<	$\frac{3}{1} = 3$
$\frac{C}{A}$:	$\frac{2.4}{1.1} = 2.18$	>	$\frac{2}{1} = 2$

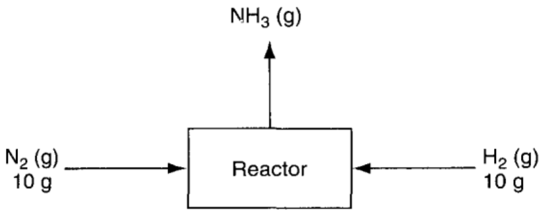
We conclude that **B** is the **limiting reactant relative to A**, and that **A** is the **limiting reactant relative** to **C**, hence **B** is the **limiting reactant** among the set of **three reactant**. In symbols we have **B < A, C > A (i.e., A < C)**, so that **B < A < C**.

Example 9.5

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



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

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

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

(b) N_2 is the limiting reactant, and that (c) H_2 is the excess reactant.

The excess H_2 = 4.960 – 3(0.357) = 3.89 g mol. To answer question (a), the maximum amount of NH_3 that can be produced is based on assuming **complete conversion** of the limiting reactant

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

9.2.3 Conversion and degree of completion

- ☒ **Conversion** is the fraction of the feed or some key material in the feed that is converted into products.
- ☒ **Conversion** is related to the **degree of completion** of a reaction namely the percentage or fraction of the limiting reactant converted into products.

Thus, **percent conversion** is

$$\%\text{ conversion} = \frac{\text{moles (or mass) of feed (or a compound in the feed) that react}}{\text{moles (or mass) of feed (or a component in the feed) introduced}} \times 100$$

<u>**For example**</u>, for the reaction equation described in **Example 9.2**, if 14.4 kg of CO_2 are formed in the reaction of 10 kg of C_7H_{16}, you can calculate what percent of the C_7H_{16} is converted to CO_2 (reacts) as follows: $C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$

C_7H_{16} equivalent to CO_2 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} in the reactants $\frac{10 \text{ kg } C_7H_{16}}{} \left| \frac{1 \text{ kg mol } C_7H_{16}}{100.1 \text{ kg } C_7H_{16}} \right. = 0.0999 \text{ kg mol } C_7H_{16}$

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

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

Conversion is equal to the extent of reaction based on CO_2 formation (i.e., the **actual extent of reaction**) divided by the extent of reaction assuming **complete reaction** of C_7H_{16} (i.e., the **maximum possible extent of reaction**).

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

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

9.2.4 Selectivity

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

For example, methanol (CH_3OH) can be converted into ethylene (C_2H_4) or propylene (C_3H_6) by the reactions

$$2\,CH_3OH \rightarrow C_2H_4 + 2H_2O$$
$$3\,CH_3OH \rightarrow C_3H_6 + 3H_2O$$

What is the selectivity of C_2H_4 relative to the C_3H_6 at 80% conversion of the CH_3OH? At 80% conversion: C_2H_4 19 mole % and for C_3H_6 8 mole %. Because the basis for both values is the same, **the selectivity** = **19/8 = 2.4 mol C_2H_4 per mol C_3H_6**.

9.2.5 Yield

No universally agreed-upon definitions exist for **yield**—in fact, quite the contrary. Here are **three** common ones:

- **Yield (based on feed)**—the amount (mass or moles) of desired product obtained divided by the amount of the key (frequently the limiting) reactant fed.
- **Yield (based on reactant consumed)**—the amount (mass or moles) of desired product obtained divided by amount of the key (frequently the limiting) reactant consumed.
- **Yield (based on theoretical consumption of the limiting reactant)**—the amount (mass or moles) of a product obtained divided by the theoretical (expected) amount of the product that would be obtained based on the limiting reactant in the chemical reaction equation if it were completely consumed.

Example 9.6

The following overall reaction to produce biomass, glycerol, and ethanol

$$C_6H_{12}O_6(\text{glucose}) + 0.118\ NH_3 \rightarrow 0.59\ CH_{1.74}N_{0.2}O_{0.45}\ (\text{biomass})$$
$$+ 0.43\ C_3H_8O_3(\text{glycerol}) + 1.54\ CO_2 + 1.3\ C_2H_5OH\ (\text{ethanol}) + 0.03\ H_2O$$

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

Solution

Basis: 0.59 g mol of biomass

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

$$\frac{1.3\ \text{g mol}\ C_2H_5OH}{1\ \text{g mol glucose}}\left|\frac{46\ \text{g}\ C_2H_5OH}{1\ \text{g mol}\ C_2H_5OH}\right|\frac{1\ \text{g mol glucose}}{180\ \text{g glucose}} = 0.332\ \text{g}\ C_2H_5OH/\text{g glucose}$$

Example 9.7

For this example, large amounts of single wall carbon nanotubes can be produced by the catalytic decomposition of ethane over Co and Fe catalysts supported on silica

$$C_2H_6 \rightarrow 2\ C + 3\ H_2 \quad (a)$$
$$\searrow C_2H_4 + H_2 \quad (b)$$

If you collect 3 g mol of H_2 and 0.50 g mol of C_2H_4, what is the selectivity of C relative to C_2H_4?

Solution

Basis: 3 g mol H_2 by Reaction (a)

0.50 g mol C_2H_4 by Reaction (b)

The 0.5 g mol of C_2H_4 corresponds to 0.50 g mol of H_2 produced in Reaction (b).

The H_2 produced by Reaction (a) = 3 - 0.50 = 2.5 g mol.

The nanotubes (the C) produced by Reaction (a) = (2/3)(2.5) = 1.67 g mol C

The selectivity = 1.67/0.50 = 3.33 g mol C/g mol C_2H_4

Example 9.8

The two reactions of interest for this example are

$$Cl_2(g) + C_3H_6(g) \rightarrow C_3H_5Cl(g) + HCl(g) \quad (a)$$

$$Cl_2(g) + C_3H_6(g) \rightarrow C_3H_6Cl_2(g) \quad (b)$$

C_3H_6 is propylene (propene) (MW = 42.08)

C_3H_5C1 is allyl chloride (3-chloropropene) (MW = 76.53)

$C_3H_6Cl_2$ is propylene chloride (1,2—dichloropropane) (MW = 112.99)

The species recovered after the reaction takes place for some time are listed in Table E9.8.

species	Cl_2	C_3H_6	C_3H_5C1	$C_3H_6Cl_2$	HCl
g mol	141	651	4.6	24.5	4.6

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

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_5C1?
e. What was the selectivity of C_3H_5C1 relative to $C_3H_6Cl_2$?
f. What was the yield of C_3H_5C1 expressed in g of C_3H_5C1 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

Figure E9.8 illustrates the process as an open-flow system. A batch process could alternatively be used.

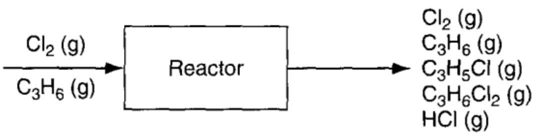


Figure E9.8

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

Reaction (a)

$$\frac{4.6 \text{ g mol } C_3H_5C1}{} \bigg| \frac{1 \text{ g mol } Cl_2}{1 \text{ g mol } C_3H_5Cl} = 4.6 \text{ g mol } Cl_2 \text{ reacts}$$

Reaction (b)

$$\frac{24.5 \text{ g mol } C_3H_6Cl_2}{} \bigg| \frac{1 \text{ g mol } Cl_2}{1 \text{ g mol } C_3H_6Cl_2} = 24.5 \text{ g mol } Cl_2 \text{ reacts}$$

Total = 4.6 + 24.5 = 29.l g mol Cl_2 reacts

Cl_2 in product = 141.0 from Table E9.8

(a) Total Cl_2 fed = 141.0 + 29.1 = 170.1 g mol Cl_2

Total C_3H_6 fed = 651.0 + 29.1 = 680.1 g mol of 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_5C1 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_5C1** 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 **$C_3H_6C_{12}$** is produced only by the **second reaction**, the **extent of reaction** of the second reaction is

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

<u>Example 9.9</u>

Five pounds of bismuth (MW=209) is heated along with one pound of sulfur (MW=32) to form Bi_2S_3 (MW=514). At the end of the reaction, the mass is extracted and the free sulfur recovered is 5% of the reaction mass. Determine

$$2\,Bi + 3\,S \longrightarrow Bi_2S_3$$

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

Solution

a. Find the Limiting reactant

Ratio in the feed

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

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

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

b. % Excess reactant

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

$$\text{\% excess Bi} = \frac{(0.0239 - 0.028)}{0.028} \times 100 = \mathbf{14.9\ \%}$$

c. We will assume that no gaseous products are formed, so that the total mass of the reaction mixture is conserved at 6 lb (5 lb Bi + 1 lb S). The free sulfur at the end of the reaction = 5%.

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

$$\text{\% Conversion} = \frac{\text{moles of feed that react}}{\text{moles of feed introduced}} \times 100$$

$$= \frac{0.0313 - 0.00938}{0.0313} \times 100 = \mathbf{70.0\ \%}$$

<u>Questions</u>

1. What is a limiting reactant?
2. What is an excess reactant?
3. How do you calculate the extent of reaction from experimental data?

<u>Answers:</u>

<u>Q.3</u> Reactant present in the least stoichiometric quantity.

<u>Q.4</u> All other reactants than the limiting reactant.

<u>Q.5</u> For a species in

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

Problems

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

$$2\,NaCl + 2\,H_2O \rightarrow 2\,NaOH + H_2 + Cl_2$$

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

4. Can you balance the following chemical reaction equation?

$$a_1NO_3 + a_2HClO \rightarrow a_3HNO_3 + a_4HCl$$

5. For the reaction in which stoichiometric quantities of the reactants are fed

$$2\,C_5H_{10} + 15\,O_2 \rightarrow 10\,CO_2 + 10\,H_2O$$

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

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

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

   The bauxite ore contains 55.4% by weight of aluminum oxide, the remainder being impurities. The sulfuric acid solution contains 77.7% pure sulfuric acid, the remainder being water. To produce crude aluminum sulfate containing 1798 lb of pure aluminum sulfate, 1080 lb of bauxite ore and 2510 lb of sulfuric acid solution are reacted.
   a. Identify the excess reactant.
   b. What percentage of the excess reactant was consumed?

c. What was the degree of completion of the reaction?

8. Two well-known gas phase reactions take place in the dehydration of ethane:

$$C_2H_6 \rightarrow C_2H_4 + H_2 \quad (a)$$

$$C_2H_6 + H_2 \rightarrow 2\,CH_4 \quad (b)$$

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) $C_9H_{18} + \frac{27}{2}O_2 \rightarrow 9\,CO_2 + 9\,H_2O$; (b) $4\,FeS_2 + 11\,O_2 \rightarrow 2Fe_2O_3 + 8\,SO_2$
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.

Supplementary Problems (Chapter Nine):

Problem 1

Gypsum (plaster of Paris : $CaSO_4 \cdot 2H_2O$) is produced by the reaction of calcium carbonate and sulfuric acid. A certain lime stone analyzes: $CaCO_3$ 96.89 %; $MgCO_3$ 1.41 %; inerts 1.70 %. For 5 metric tons of limestone reacted completely, determine:

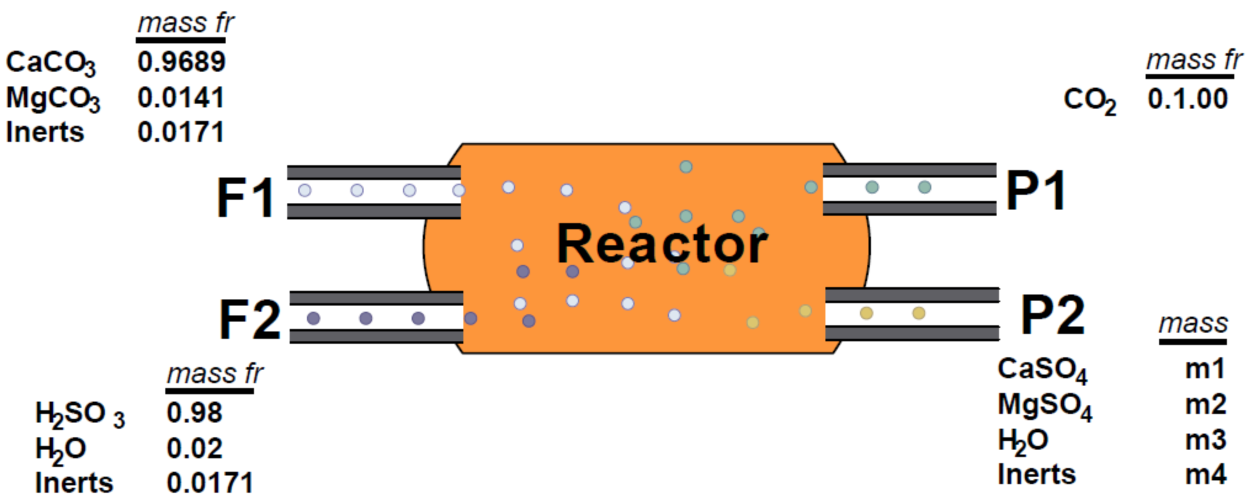
a. kg of anhydrous gypsum ($CaSO_4$) produced.
b. kg of sulfuric acid solution (98 wt%) required.
c. kg of carbon dioxide produced.
(MW : $CaCO_3$ 100.1; $MgCO_3$ 84.32; H_2SO_4 98; $CaSO_4$ 136; $MgSO_4$ 120; H_2O 18; CO_2 44)

Solution

The problem involves 2 reactions. Both calcium carbonate and magnesium carbonate react with sulfuric acid. The stoichiometric equations are

$$CaCO_3 + H_2SO_4 \text{------>} CaSO_4 + H_2O + CO_2 \qquad (1)$$

$$MgCO_3 + H_2SO_4 \text{------>} MgSO_4 + H_2O + CO_2 \qquad (2)$$



Basis : 5000 kg limestone

a. $CaSO_4$ produced

$$\frac{5000\,kg\,limestone}{} \left| \frac{96.89\,kg\,CaCO_3}{100\,kg\,limestone} \right| \frac{1\,kgmol\,CaCO_3}{100.1\,kg\,CaCO_3} \left| \frac{1\,kgmol\,CaSO_4}{1\,kgmol\,CaCO_3} \right| \frac{136\,kg\,CaSO_4}{1\,kgmol\,CaSO_4}$$

= 6600 kg $CaSO_4$

b. Sulfuric acid required

Both $CaCO_3$ and $MgCO_3$ react with sulfuric acid in a 1 to 1 molar ratio.

$$\frac{5000\,kg\,limestone}{} \left| \frac{96.89\,kg\,CaCO_3}{100\,kg\,limestone} \right| \frac{1\,kg\,mol\,CaCO_3}{100.1\,kg\,CaCO_3} \left| \frac{1\,kg\,mol\,H_2SO_4}{kgmol\,CaCO_3} \right| \frac{98\,kg\,H_2SO_4}{kgmol\,H_2SO_4}$$

= 4740 kg H_2SO_4

$$\frac{5000\,kg\,limestone}{} \left| \frac{1.41\,kg\,MgCO_3}{100\,kg\,limestone} \right| \frac{1\,kg\,mol\,MgCO_3}{84.32\,kg\,MgCO_3} \left| \frac{1\,kg\,mol\,H_2SO_4}{kg\,mol\,MgCO_3} \right| \frac{98.0\,kg\,H_2SO_4}{kg\,mol\,H_2SO_4}$$

= 81.94 kg H_2SO_4

total acid required = 4739.9 + 81.94 kg = 4822 kg 100 % acid.

We need to correct for the fact that acid is available as a 98 % solution.

$$\frac{4821.84\,kg\,H_2SO_4}{} \left| \frac{100\,kg\,acid\,solution}{98.0\,kg\,H_2SO_4} \right. = \mathbf{4920\,kg\,H_2SO_4\,solution}$$

c. Carbon dioxide generated

Both $CaCO_3$ and $MgCO_3$ react with sulfuric acid to produce carbon dioxide.

$$\frac{5000\,kg\,limestone}{} \left| \frac{96.83\,kg\,CaCO_3}{100\,kg\,CaCO_3} \right| \frac{1\,kg\,mol\,CaCO_3}{100.1\,kg\,CaCO_3} \left| \frac{1\,kg\,mol\,CO_2}{1\,kg\,mol\,CaCO_3} \right| \frac{44\,kg\,CO_2}{1\,kg\,mol\,CO_2} +$$

$$\frac{5000\,kg\,limestone}{} \left| \frac{1.41\,kg\,MgCO_3}{100\,kg\,MgCO_3} \right| \frac{1\,kg\,MgCO_3}{84.32\,kg\,MgCO_3} \left| \frac{1\,kg\,mol\,CO_2}{1\,kg\,mol\,MgCO_3} \right| \frac{44\,kg\,CO_2}{1kg\,mol\,CO_2}$$

= 2128.1 + 36.8 = **2165 kg CO_2**

Problem 2

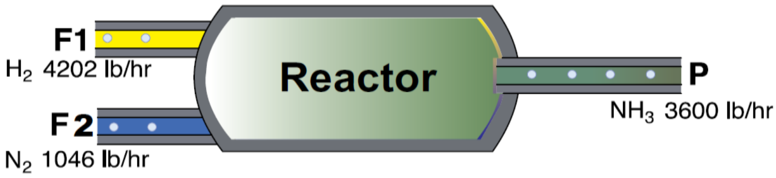
The synthesis of ammonia proceeds according to the following reaction

$$N_2 \quad + \quad 3\,H_2 \quad \text{----->} \quad 2\,NH_3$$

In a given plant, 4202 lb of nitrogen and 1046 lb of hydrogen are fed to the synthesis reactor per hour. Production of pure ammonia from this reactor is 3060 lb per hour.

a. What is the limiting reactant.
b. What is the percent excess reactant.
c. What is the percent conversion obtained (based on the limiting reactant).

Solution



a.

$$\frac{4202 \text{ lb } N_2}{} \left| \frac{1 \text{ lb mol } N_2}{28 \text{ lb } N_2} \right| \frac{2 \text{ lb mol } NH_3}{1 \text{ lb mol } N_2} = 300 \text{ lb mol } NH_3$$

$$\frac{1046 \text{ lb } H_2}{} \left| \frac{1 \text{ lb mol } H_2}{2 \text{ lb } H_2} \right| \frac{2 \text{ lb mol } NH_3}{3 \text{ lb mol } H_2} = 348.6 \text{ lb mol } NH_3$$

If all of the N_2 were to react, 300 lb mol of ammonia would be produced while if all of the hydrogen were to react, 348.6 lb mol ammonia would be produced. **N_2 is the limiting reactant.**

b. H_2 required : based on the limiting reactant

$$\frac{4202 \text{ lb } N_2}{} \left| \frac{1 \text{ lb mol } N_2}{28 \text{ lb } N_2} \right| \frac{3 \text{ lb mol } H_2}{1 \text{ lb mol } N_2} = 450 \text{ lb mol } H_2 \text{ required}$$

H_2 available :

$$\frac{1046 \text{ lb } H_2}{} \left| \frac{1 \text{ lb mol } H_2}{2 \text{ lb } H_2} \right. = 523 \text{ lb mol } H_2$$

$$\% \text{ excess reactant} = \frac{\text{mol in excess}}{\text{mol required to react with limiting reactant}} \times 100$$

$$\% \text{ excess } H_2 = \frac{(523 - 450)}{450} \times 100 = \mathbf{16.2\ \%}$$

c.

$$\text{Percentage conversion} = \frac{\text{moles (or mass) of feed that react}}{\text{moles (or mass) of feed introduced}} \times 100$$

$$N_2 \text{ reacted} = \frac{3060 \text{ lb } NH_3}{} \left| \frac{1 \text{ lb mol } NH_3}{17 \text{ lb } NH_3} \right| \frac{1 \text{ lb mol } N_2}{2 \text{ lb mol } NH_3} \left| \frac{28 \text{ lb } N_2}{1 \text{ lb mol } N_2} \right. = 2520 \text{ lb } N_2$$

$$\% \text{ conversion} = \frac{2520 \text{ lb}}{4202 \text{ lb}} \times 100 = \mathbf{60.0\ \%}$$