THE CHEMICAL REACTION EQUATION AND STOICHIOMETRY

9.1 Stoichiometry

- Stoichiometry provides a quantitative means of relating the amount of products produced by chemical reaction(s) to the amount of reactants.
- You should take the following steps in solving stoichiometric problems:
  - Make sure the chemical equation is correctly balanced.
  - Use the proper degree of completion for the reaction.
  - Use molecular weights to convert mass to moles for the reactants and products, and vice versa.

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- Use the coefficients in the chemical equation to obtain the molar amounts of products produced and reactants consumed by the reaction.

Example:

$$CH_4 + O_2 \longrightarrow CO_2 + H_2O$$

Is the following equation balanced?

Solution: NO

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

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Example:

$$C_7H_{16}(\ell) + 11\,O_2(g) \rightarrow 7\,CO_2(g) + 8\,H_2O(g)$$

- The **stoichiometric coefficients** in the chemical reaction equation tell you the relative amounts of moles of chemical species that react and are produced by the reaction.
- 1 mole (*not* lb, or kg) of heptane will react with 11 moles of oxygen to give 7 moles of carbon dioxide plus 8 moles of water
- 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 (7/8) each mole of CO_2.

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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_{16}

$$C_7H_{16}(\ell) + 11\ O_2(g) \rightarrow 7\ CO_2(g) + 8\ H_2O(g)$$

Solution:

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

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Example: The primary energy source for cells is the aerobic catabolism (oxidation) of glucose ($C_6H_{l2}O_6$, 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:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

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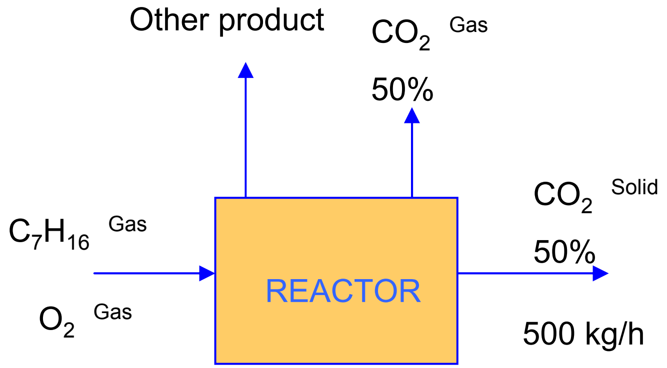
Example: In the combustion of heptane, CO_2 is produced. Assume that you want to produce 500 kg of dry ice per hour, and that 50% of the CO_2 can be converted into dry ice. How many kilograms of heptane must be burned per hour?



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Solution:

$$C_7H_{16}(\ell) + 11\,O_2(g) \rightarrow 7\,CO_2(g) + 8\,H_2O(g)$$

Basis: 1 h (500 kg of dry ice)

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

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Example: **A** limestone analyses (weight %)

CaC03	92.89%
MgCO3	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?

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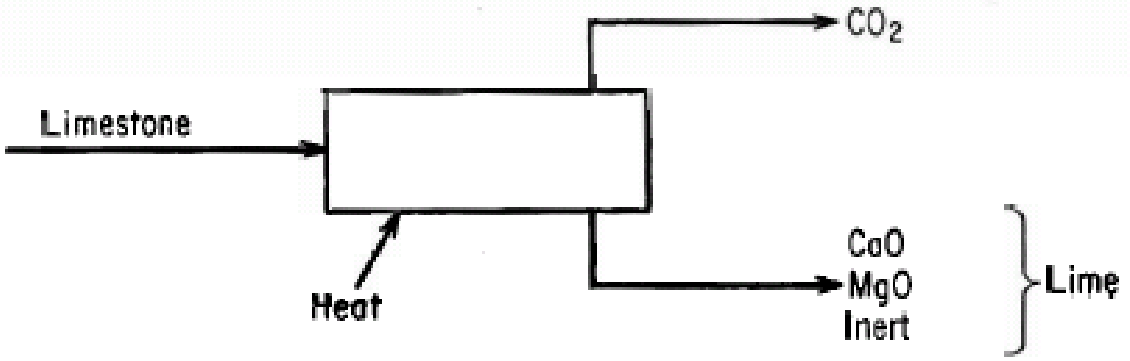
Solution:

Step 1:

- The carbonates are decomposed to oxides.

Step 2,3:



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Step 4:

$$CaCO_3 \rightarrow CaO + CO_2$$

$$MgCO_3 \rightarrow MgO + CO_2$$

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

Step 5:

Basis: 100 lb of limestone

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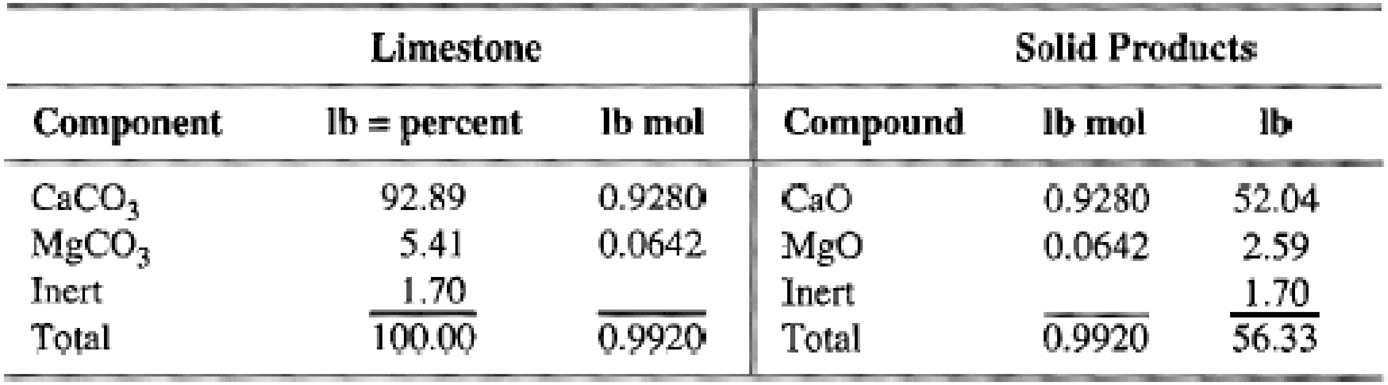
Step 6,7,8,9:



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

$$\begin{array}{c|c|c|c} \text{92.89 lb } CaCO_3 & \text{1 lb mol } CaCO_3 & \text{1 lb mol CaO} & \text{56.08 lb CaO} \\ \hline & \text{100.1 lb } CaCO_3 & \text{1 lb mol } CaCO_3 & \text{1 lb mol CaO} \end{array} = \text{52.04 lb CaO}$$

$$\begin{array}{c|c|c|c} \text{5.41 lb } MgCO_3 & \text{1 lb mol } MgCO_3 & \text{1 lb mol MgO} & \text{40.32 lb MgO} \\ \hline & \text{84.32 lb } MgCO_3 & \text{1 lb mol } MgCO_3 & \text{1 lb mol MgO} \end{array} = \text{2.59 lb MgO}$$

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The production of CO2 is:

0.9280 lb mol CaO is equivalent to 0.9280 lb mol CO2

0.0642 lb mol MgO is equivalent to <u>0.0642</u> lb mol CO2

Total 0.992 lb mol CO2

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

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

$$\text{(b)}\quad \text{CO}_2\ \text{recovered} = \frac{44.65\ \text{lb CO}_2}{100\ \text{lb limestone}} = 0.447\ \text{lb CO}_2\text{/lb limestone}$$

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

9.2-1 Extent of Reaction

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

Example:

$$2CO + O_2 + 2CO_2$$

If 20 moles of CO are fed to a reactor with 10 moles of O_2 and form 15 moles of CO_2, calculate the extent of reaction from the amount of CO_2 that is produced?

Solution:

The value of the change in the moles of CO_2 is: 15 - 0 = 15.

The value of the stoichiometric coefficient for the CO_2 is: 2 mol/mol reacting

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$$\frac{(15 - 0)\ \text{mol CO}_2}{2\ \text{mol CO}_2\ /\text{moles reacting}} = 7.5\ \text{moles reacting}$$

- The extent of reaction is defined as follows:

$$\xi = \frac{n_i - n_{io}}{v_\text{i}}$$

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)

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or

$$ni = n_{io} + \xi\, v_{\mathrm{i}}$$

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9.2- 2 Limiting and Excess Reactants

- **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.**

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

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Example:

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

- 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.
- The amount of the **excess reactant** O_2 would be 12 g mol less the 11 gmole needed to react with 1 g mol of C_7H_{16}, or 1 g mol of O_2.
- Therefore, if the reaction were to go to completion, the amount of product produced would be controlled by the amount of the limiting reactant.

How to determine the limiting reactant?

- you can determine the maximum extent of reaction, ξ^{max}, each reactant based on **the complete reaction** of the reactant. **The reactant with the smallest maximum extent of reaction is the limiting reactant.**

Example: what is the limiting reactant for the following reaction

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

if 1 g mol of C_7H_{16} react with 12 g mole of O_2?

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Solution:

$$\xi^{\max}\text{ (based on O2)} = \frac{0\text{ g mol } O_2 - 12\text{ g mol } O_2}{-11\text{ g mol } O_2/\text{ moles reacting}} = 1.09\text{ moles reacting}$$

$$\xi^{\max}\text{ (based on } C_7H_{16}) = \frac{0\text{ g mol } C_7H_{16} - 1\text{ g mol } C_7H_{16}}{-1\text{ g mol } C_7H_{16}\text{ / moles reacting}} = 1.0\text{ moles reacting}$$

Therefore, C_7H_{16} is the limiting reactant and O_2 is the excess reactant.

9.2- 3 Conversion and degree of completion

- **Conversion** is the fraction of the feed or some *key* material in the feed that converted into products

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

- **Degree of completion** is the percentage or fraction of the limiting reactant converted into products.

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.

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9.2-5 Yield

- **yield** (based on feed) is 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) is 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) is 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(s) if it were completely consumed.

EXAMPLE 9.8 Calculation of Various Terms Pertaining to Reactions

Semenov (*Some Problems in Chemical Kinetics and Reactivity*, Princeton Univ. Press (1959), Vol II, pp. 39–42) described some of the chemistry of allyl chlorides. The two reactions of interest for this example are

$$Cl_2(g) + C_3H_6(g) \rightarrow C_3H_5Cl(g) + HCl(g) \qquad \text{(a)}$$

$$Cl_2(g) + C_3H_6(g) \rightarrow C_3H_6Cl_2(g) \qquad \text{(b)}$$

C_3H_6 is propylene (propene) (MW = 42.08)
C_3H_5Cl 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.

TABLE E9.8

Species	g mol
Cl_2	141.0
C_3H_6	651.0

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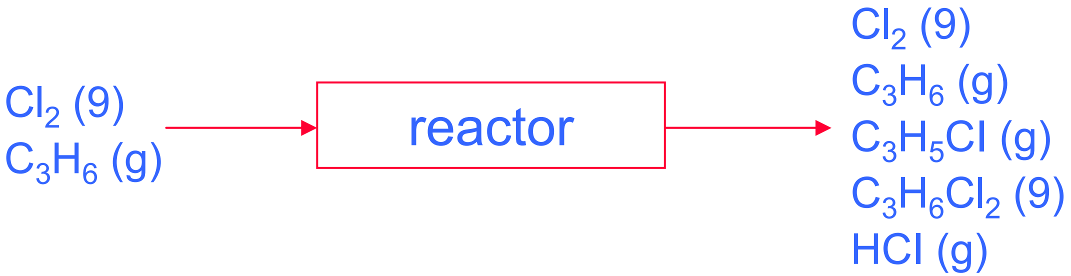
Solution

Steps 1,2,3, and 4



Cl_2 (9)
C_3H_6 (g)

reactor

Cl_2 (9)
C_3H_6 (g)
C_3H_5Cl (g)
$C_3H_6Cl_2$ (9)
HCl (g)

Step 5

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

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Steps 7,8, and 9

Use the chemical equations to calculate the moles of species in the feed.

Reaction (a)

$$\frac{4.6\text{ g mol }C_3H_5Cl}{}\;\Bigg|\;\frac{1\text{ g mol }Cl_2}{1\text{ g mol }C_3H_5Cl} = 4.6\text{ g mol }Cl_2\text{ reacts}$$

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	$\underline{29.1}$ g mol Cl_2 reacts
Cl_2 in product	141.0
Total Cl_2 fed	$\underline{170.1}$

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- If 29.1 g mol Cl_2 reacts by Reactions (a) and (b), 29.1 g mol of C_3H_6 must react. Since 651.0 g mol of C_3H_6 exist in the product

651.0 + 29.1 = 680.1 g mol of C_3H_6 were fed to the reactor.

(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

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

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

therefore, 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:

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

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(e) The selectivity is:

$$\frac{4.6 \text{ g mol } C_3H_5Cl}{24.5 \text{ g mol } C_3H_6CI_2} = 0.19 \frac{\text{g mol } C_3H_5Cl}{\text{g mol } C_3H_6C1_2}$$

(f) The yield is:

$$\frac{(76.53)\,(4.6) \text{ g } C_3H_5Cl}{(42.08)\,(680.1) \text{ g } C_3H_6CI_2} = 0.012 \frac{\text{g } C_3H_5Cl}{\text{g } C_3H_6}$$

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

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

Because $C_3H_6C1_2$ is produced only by the second reaction, the extent of I reaction of the second reaction is

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

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(h) Mole efficiency in the waste:

Entering Cl: (170.1)(2) = 340.2 g mol

Exiting Cl in HCl : 4.6 g mol

$$\frac{\text{mole of chlorine in waste}}{\text{mole of chlorine entering}} = \frac{4.6}{340.2} = 0.0135$$

Mole efficiency of the product = 1 - 0.0135 = 0.987