Lecture no. 9

1.9 THE CHEMICAL EQUATION AND STOICHIOMETRY

As you already know, the chemical equation provides a variety of qualitative and quantitative information essential for the calculation of the combining weights (mass) of materials involved in a chemical process. Take, for example, the ombustion of heptane as shown below. What can we learn from this equation?

$$C_7H_{16} + 11\ 0_2 \ == \ 7\ CO2_2 + 8\ H_2O \qquad (1.27)$$

It tells us about stoichiometric ratios. First, make sure that the equation is balanced! Then you can see that 1 mole *(not* Ibm 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 Ib mol, g mol, kg mol, or any other type of mole, as shown in Fig. 1.15. One mole of CO, is formed from each t mole of C7H16• Also, 1 mole of H,O is formed

C_7H_{16}	+	$11O_2$	$\longrightarrow$	$7CO_2$	+	$8H_2O$
			Qualitative information			
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
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
1(100) g of C_7H_{16}	+	11(32) g of O_2	=	7(44) g of CO_2	+	8(18) g of H_2O
100 g		352 g		308 g		144 g
	452 g		=		452 g	
	452 kg		=		452 kg	
	452 ton		=		452 ton	
	452 lb		=		452 Ib	

Figure 1.15 Application of the chemical equation.

with each 7/8 mole of CO_2. Thus the equation tells 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 0_2 and so on.

Stoichiometry (stoi-ki-om-e-tri)'? 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 (Ibm, kg) rather than moles, you should use the following method in solving problems involving the use of chemical equations: (I) 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 ease 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

1 kg mole $\qquad\qquad$ 7 kg mole

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

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

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, CO2 is produced. Assume that you want to produce 500 kg of dry ice per hour and that 50% of the CO2 can be converted into dry ice, as shown in Fig. El.27. Howmany kilograms of heptanemustbe burned per hour?

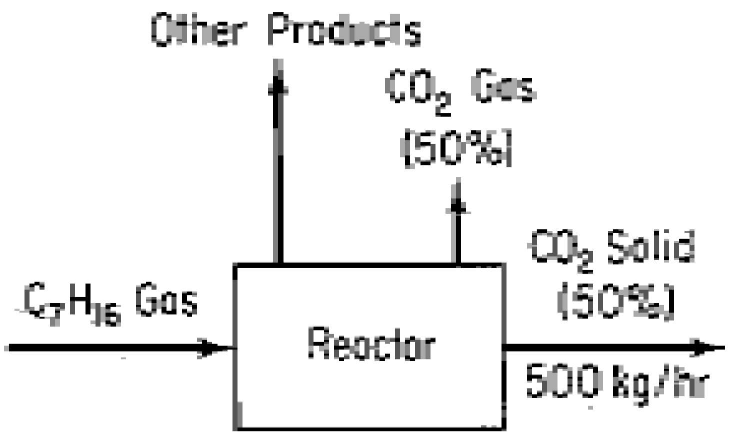

Figure E1.27

Solution

Basis: 500 kg of dry ice (or I 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 I hr, 325 kg of C,H16 must be burned per hour. Note that kiiograms are first converted to moles, then the chemical equation is applied, and finally moles are converted to kilograms again for thefinal 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:

$$2Na_2SO_3 + 0_2 == 2Na_2S0_4$$

How many pounds of sodium sulfite are theoretically required (for complete reaction) to remove the oxygen from 8,330,000 Ib of water (106 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.

Solution

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

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

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

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, can be recovered per pound of limestone?
(c) How many pounds of limestone are needed to make I 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 CO2 has been driven off. Next, draw a picture of what is going on in this process. See Fig. E1.29.

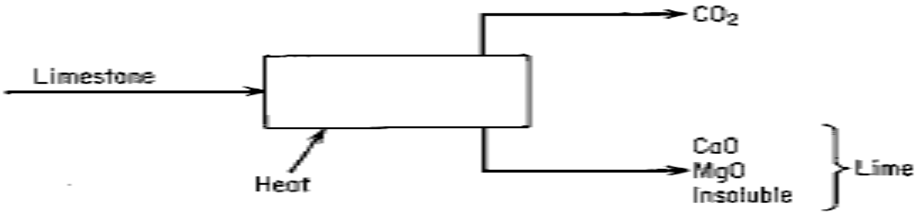

Figure E1.29

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

An assumption implicit in the calculations above is that the reaction takes place exactly as written in the equation and proceeds to 100% completion. When reactants, products, or degree of completion of the actual reaction differ from the assumptions of the equation, additional data must be made available to predict the outcome of reactions.

In industrial reactors you will rarely find exact stoichiometric amounts of materials used. To make a desired reaction take place or to use up a costly reactant, excess reactants are nearly always used. This excess material comes out together with, or perhaps separately from, the product-and sometimes can be used again. Even if stoichiometric quantities of reactants are used, but if the reaction is not complete or there are side reactions, the products will be accompanied by unused reactants as well as side products. In these circumstances some new definitions!' must be understood:

(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 C7H'6 and 12 g mol of 0, are mixed, C7H'6 would be the limiting reactant even if the reaction does not take place.

As a shortcut to determining the limiting reactant, all you have to do is to calculate the mole ratio(s) of the reactants and compare each ratio with the corresponding ratio of the coefficients of the reactants in the chemical equation thus:

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

If more than two reactants are present, you have to use one reactant as the reference substance, calculate the mole ratios of the other reactants in the feed relative to the reference, make pairwise comparisons versus the analogous ratios in the chemical
mo es reqUIre to react With limiting reactant
equation, and rank each compound. For example, given the reaction

$$A + 3B + 2C \longrightarrow \text{products}$$

and that 1.1 moles of *A*, 3.2 moles of *B*, and 2.4 moles of C are fed as reactants into the reactor, 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 limitingnreactant relative to C, hence *B* is the limiting reactant among the set of three reactants. In symbols we have $B < A$, $C > A$ (i.e., $A < C$), so that $B < A < C$.

(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 availablemoles 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 avail**able 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,

Air requirements for combustion vary with the need to enSure full utilization of the fuel's heating value but not generate excessive air pollutants. The excess air required in practice depends on the type of fuel, the furnace, and the burner. Fuel oil, for instance, requires 5 to 20% excess air depending on burner design. Excess air is recognized as a routine measure of heater performance.

Three other terms that are used in connection with chemical reactions have less clear-cut definitions: conversion, selectivity, and yield. No universally agreed upon definitions exist for these terms-in fact, quite the contrary. Rather than cite all the possible usages of these terms, many of which conflict, we shall define them as follows:

(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 calcnlations 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:

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?

The employment of these concepts can best be illustrated by examples.