Lecture Nine

(THE CHEMICAL REACTION EQUATION AND STOICHIOMETRY)

9.1 Other Terminologies for Applications of Stoichiometry

9.1.1 Limiting and Excess Reactants

9.1.2 Conversion and degree of completion

9.1.3 Selectivity

9.1.3 Yield

9.2 Solved Examples

Your Objectives in Studying this Lecture are:

- Write and balance chemical reaction equations.
- Define excess (الفائض) reactant, limiting reactant, conversion, degree of completion (الأنتقائية), yield (الأنتاجية), yield (الأنتاجية).

9.1 Other Terminologies for Applications of Stoichiometry

9.1.1 Limiting and Excess Reactants

<u>The limiting reactant</u> 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.

Or, is the reactant which is present in the smallest stoichiometric amount. *Or,* The reactant with the smallest maximum extent of reaction.

Excess reactants is a reactant in excess of limiting reactant.



(9.1)

EXAMPLE-9.1: Using the chemical reaction equation

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

if **1** g mol of C_7H_{16} and **12** g mol of O_2 are mixed, C_7H_{16} would be the limiting reactant even if the reaction does not take place. The amount of the excess reactant O_2 would be 12 g mol less the 11 g mole 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.

As a straightforward way of determining the limiting reactant, We can determine the *maximum extent of reaction*, ξ^{max} , for each reactant based on the complete reaction of the reactant. <u>*Calculate the maximum extent*</u> <u>of reaction?</u>

<u>Solution</u>

$$\xi^{\max} \text{ (based on O_2)} = \frac{0 \text{ g mol } \text{O}_2 - 12 \text{ g mol } \text{O}_2}{-11 \text{ g mol } \text{O}_2/\text{moles reacting}} = 1.09 \text{ moles reacting}$$

$$\xi^{\max} \text{ (based on C_7H_{16})} = \frac{0 \text{ g mol } \text{C}_7\text{H}_{16} - 1 \text{ g mol } \text{C}_7\text{H}_{16}}{-1 \text{ g mol } \text{C}_7\text{H}_{16}/\text{moles reacting}} = 1.00 \text{ moles reacting}$$

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

As an alternate to determining the limiting reactant, all you have to do is to calculate the mole ratios of the reactants and compare each ratio with the corresponding ratio of the coefficients of the reactants in the chemical equation thus:

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

EXAMPLE-9.2 Consider the following reaction

$$A + 3B + 2C \rightarrow Products$$

Calculate the maximum extent of reaction?

<u>Solution</u>

<u>If the feed</u> 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;

$$\xi^{\text{max}}$$
 (based on A) = $\frac{-1.1 \text{ mol A}}{-1}$ = 1.1
 ξ^{max} (based on B) = $\frac{-3.2 \text{ mol B}}{-3}$ = 1.07
 ξ^{max} (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. In this case we have *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 pair wise comparisons versus the analogous ratios in the chemical equation, and rank ($(in, j_{\ell}, j_{\ell$

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

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 reactants. In symbols we have $\mathbf{B} < \mathbf{A}$, $\mathbf{C} > \mathbf{A}$ (i.e., $\mathbf{A} < \mathbf{C}$), so that $\mathbf{B} < \mathbf{A} < \mathbf{C}$.

EXAMPLE-9.3: Consider Calculation of the Limiting and Excess Reactants Given the Mass of Reactants

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 NH₃ that can be produced?

(b) What is the limiting reactant?

(c) What is the excess reactant?

Solution

You are asked to calculate the limiting reactant, and use a chemical reaction equation to calculate the NH_3 produced. At room temperature and pressure no reaction will occur, but you are asked to calculate what would result if the reaction were to occur (as it does under other conditions of temperature and pressure).

Look at Figure E9.5.



Figure E9.5

Next, write down the chemical equation, and get the molecular weights:

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

The next step is to determine the limiting reactant by calculating the maximum extent of reaction based on the complete reaction of N_2 and H_2 .

 ξ^{max} (based on N₂) = $\frac{-0.357 \text{ g mol N}_2}{-1 \text{ g mol N}_2/\text{moles reacting}} = 0.357$ moles reacting

$$\xi^{\text{max}}$$
 (based on H₂) = $\frac{-4.960 \text{ g mol H}_2}{-3 \text{ g mol H}_2/\text{moles reacting}} = 1.65$ moles reacting

You can conclude that (b) N_2 is the limiting reactant, and that (c) H_2 is the excess reactant. The excess H_2 is 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

$$\frac{0.357 \text{ g mol } \text{N}_2}{1 \text{ g mol } \text{N}_2} \left| \frac{2 \text{ g mol } \text{NH}_3}{1 \text{ g mol } \text{N}_2} \right| \frac{17.02 \text{ g NH}_3}{1 \text{ g mol } \text{NH}_3} = 12.2 \text{ g NH}_3$$

Finally, you should check your answer by working from the answer to the given reactant, or, alternatively, by adding up the mass of the NH_3 and the mass of excess H_2 . What should the sum be? 9.

1.2 Conversion and degree of completion

<u>Conversion</u> is the fraction of the feed or some key material in the feed that is converted into products. <u>Degree of completion</u> of a reaction namely the percentage or fraction of the limiting reactant converted into products.

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

EXAMPLE-9.4 the combustion of heptane

The combustion of heptane takes place according to the following reaction equation;

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

If 14.4 kg of CO₂ 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 CO₂ (reacts) as follows: Solution

$$\frac{C_{7}H_{16} \text{ equivalent}}{\text{to } CO_{2} \text{ in the product}} \frac{14.4 \text{ kg } CO_{2}}{44.0 \text{ kg } CO_{2}} \left| \frac{1 \text{ kg } \text{mol } CO_{2}}{7 \text{ kg } \text{mol } CO_{2}} \right| = 0.0468 \text{ kg } \text{mol } C_{7}H_{16}$$

$$C_{7}H_{16} \text{ in the reactants} \qquad \frac{10 \text{ kg } C_{7}H_{16}}{100.1 \text{ kg } C_{7}H_{16}} \left| \frac{1 \text{ kg } \text{mol } C_{7}H_{16}}{100.1 \text{ kg } C_{7}H_{16}} \right| = 0.0999 \text{ kg } \text{mol } C_{7}H_{16}$$

% conversion = $\frac{0.0468 \text{ mol reacted}}{0.0999 \text{ kg mol fed}} 100 = 46.8\% \text{ of the } C_7 H_{16}$

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).

$$\operatorname{conversion} = \frac{\operatorname{extent of reaction that actually occurs}}{\operatorname{extent of reaction that would occur if complete reaction took place} = \frac{\xi}{\xi^{\max}} \qquad (9.2)$$

$$\zeta_{CO_2} = \frac{0.327 - 0}{7} = 0.0467 \operatorname{mols}$$

$$\zeta_{TM_{16}} = \frac{0 - 0.1}{-1} = 0.1 \operatorname{mols}$$

$$% \operatorname{Conversion} = \frac{0.0468}{0.1} \times 100 = 46.8\% C_7 H_{16}$$

<u>Selectivity</u> 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.

$$Selectivity = \frac{desired}{undesired}$$
(9.3)

EXAMPLE- 8 Converted of methanol

Methanol (CH₃OH) can be converted into ethylene (C₂H₄) or propylene (C₃H₆) by the reactions

 $2CH_{3}OH \longrightarrow C_{2}H_{4} + 2 H_{2}O$ $3CH_{3}OH \longrightarrow C_{3}H_{6} + 3 H_{2}O$

to be significantly greater than the reactants. Examine the data in Figure 9.1 for the concentrations of the products of the reactions. What is the selectivity of C_2H_4 relative to the C_3H_6 at 80% conversion of the CH₃OH? Proceed upward at 80% conversion to get for C_2H_4 =19 mole % and for C_3H_6 = 8 mole %. Because the basis for both values is the same.



Figure 9.1: Products from the conversion of ethanol.

<u>Solution</u> : The selectivity is $19/8 = 2.4 \text{ mol } C_2H_4$ per mol C_3H_6 .

9.1.3 Yield

<u>Selectivity</u> is the ratio of the moles of a particular (usually the desired)

- <u>yield (based on feed)</u> :The amount (mass or moles) of desired product obtained divided by the amount of the key (frequently the limiting) reactant fed.
- <u>yield (based on reactant consumed)</u>: The amount (mass or moles) of desired product obtained divided by amount of the key (frequently the limiting) reactant consumed.
- *<u>vield (based on theoretical consumption of the limiting reactant)</u>: 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.*

Lecture Eight and Nine/Practical

(THE CHEMICAL REACTION EQUATION AND STOICHIOMETRY)

PROBLEMS

<u>P.1</u> 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. Two reactions of interest for this example are

$$Cl_2(g) + C_3H_6(g) \longrightarrow C_3H_5Cl(g) + HCl(g)$$
 (a)

$$Cl_2(g) + C_3H_6(g) \longrightarrow C_3H_6Cl_2(g)$$
 (b)

 $C_{3}H_{6}$ is propylene (propene) (MW = 42.08) $C_{3}H_{5}C1$ is allyl chloride (3-chloropropene) (MW = 76.53) $C_{3}H_{6}C1_{2}$ is propylene chloride (1,2—dichloropropane) (MW = 112.99)

The species recovered after the reaction takes place for some time are listed in Table 1.

Table - 1				
Species	g mol			
$Cl_2 C_3H_6 C_3H_5Cl C_3H_6Cl_2 HCl$	141.0 651.0 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 $C1_2$ 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 $C_3H_6C1_2$?
- 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?
- h. In the application of green chemistry, you would like to identify classes of chemical reactions that have the potential for process improvement, particularly waste reduction. In this example the waste is HCl (g). The Cl₂ is not considered to be a waste because it is recycled. What is the mole efficiency, i.e., the fraction of an *element* in the entering reactants that emerges in the exiting products, for chlorine?

Solution

Steps 1, 2, 3, and 4

Examination of the problem statement reveals that the amount of feed is not given, and consequently you must first calculate the g mol fed to the reactor even if the amounts were not asked for. The molecular weights are given. Figure E9.8 illustrates the process as an open-flow system. A batch process could alternatively be used.



Step 5

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

Steps 7, 8, and 9

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

Reaction (a)

$$\frac{4.6 \text{ g mol } \text{C}_3\text{H}_5\text{C}1}{1 \text{ g mol } \text{C}_3\text{H}_5\text{C}1} = 4.6 \text{ g mol } \text{C}1_2 \text{ reacts}$$

Reaction (b)

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

$$Total \qquad \frac{29.1 \text{ g mol } Cl_2 \text{ reacts}}{141.0}$$
(a) Total Cl_2 fed 170.1

From the chemical equations you can see that if 29.1 g mol $C1_2$ 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,

 $651.0 + 29.1 = 680.1 \text{ g mol of } C_3H_6$

were fed to the reactor.

You can check those answers by adding up the respective g mol of C1, C, and H in the product and comparing the values with that calculated in the feed:

C1	$\frac{\text{In product}}{2(141.0) + 1(4.6) + 2(2)}$	$\frac{\text{In product}}{2(141.0) + 1(4.6) + 2(24.5) + 1(4.6) = 340.2}$		
C	3(651) + 3(4.6) + 3(24)	3(651) + 3(4.6) + 3(24.5) = 2040.3		
H	6(651) + 5(4.6) + 6(24)	6(651) + 5(4.6) + 6(24.5) + 1(4.6) = 4080.6		
C1	$\frac{\text{In feed}}{2(170.1)} = 340.2$	ОК		
C	3(680.1) = 2040.3	ОК		
H	6(680.1) = 4080.6	ОК		

We will not go through detailed steps for the remaining calculations, but simply determine the desired quantities based on the data prepared for Part (a).

(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

 ξ^{max} (based on C₃H₆) = $\frac{-680.1 \text{ g mol C}_3\text{H}_6}{-1 \text{ g mol C}_3\text{H}_6/\text{moles reacting}} = 680.1 \text{ moles reacting}$

 ξ^{max} (based on Cl₂) = $\frac{-170.1 \text{ g mole Cl}_2}{-1 \text{ g mol Cl}_2/\text{moles reacting}} = 170.1 \text{ moles reacting}$

Thus, C3H6 was the excess reactant and C12 the limiting reactant.

(d) The fraction conversion of C₃H₆ to C₃H₅Cl was

$$\frac{4.6 \text{ g mol } C_3 H_6 \text{ that reacted}}{680.1 \text{ g mol } C_3 H_6 \text{ fed}} = 6.76 \times 10^{-3}$$

(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

$$\frac{(76.53)(4.6)g C_3 H_5 Cl}{(42.08)(680.1)g C_3 H_6} = 0.012 \frac{g C_3 H_5 Cl}{g C_3 H_6}$$

(g) Because C₃H₅Cl 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 $C_3H_6Cl_2$ is produced only by the second reaction, the extent of reaction of the second reaction is

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

(h) Mole efficiency in the waste:

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

Exiting C1 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

It would be difficult to find a better reaction pathway to obtain the indicated products. Of course, the processing of the HCl (g) must be considered.