Lecture 4.

Chemical Equation and Stoichiometry

What can we learn from a chemical equation?

$$C_7H_{16} + 11\ O_2 <======> 7\ CO_2 + 8\ H_2O$$

1. What information can we get from this equation?
2. What is the first thing we need to check when using a chemical equation?
3. What do you call the number that precedes each chemical formula?
4. How do we interpret those numbers?

What can we learn from a chemical equation?

1. A chemical equation provides both qualitative and quantitative information

2. Before using a chemical equation, make sure that it is balanced.

3. The number that precedes a compound is known as the stoichiometric coefficient.

4. The stoichiometric coefficient may be interpreted as number of moles or molecules.

The Stoichiometric Coefficient

The stoichiometric coefficients tell us the mole (not mass) relationships (stoichiometric ratios) of the compounds participating in the reaction.

For the chemical equation shown previously,

1 gmol of C_7H_{16} reacts with 11 gmol of O_2

to yield

7 gmol of CO_2 and 8 gmol of H_2O

The Stoichiometric Coefficient

Is it possible to establish the mass relationships from the stoichiometric coefficients?

Consider:

If 10 kg of C_7H_6 react completely with the stoichiometric quantity, how many kg of CO_2 will be produced?

$$m_{CO_2} = 10\,kg\,C_7H_{16}\left(\frac{1\,kmol\,C_7H_{16}}{100\,kg\,C_7H_{16}}\right)\left(\frac{7\,kmol\,CO_2}{1\,kmol\,C_7H_{16}}\right)\left(\frac{44\,kg\,CO_2}{1\,kmol\,CO_2}\right)$$

$$m_{CO_2} = 30.8\,kg\,CO_2$$

Example 4.1 - Stoichiometry

A limestone analysis shows the following composition:

$CaCO_3$	**92.89%**
$MgCO_3$	**5.41%**
Inerts	**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 (mixture of CaO, MgO, and inerts)?

Example 4.1 - Stoichiometry

Chemical Equations:

$$\mathbf{CaCO_3 \Longleftrightarrow CaO + CO_2}$$

$$\mathbf{MgCO_3 \Longleftrightarrow MgO + CO_2}$$

Molecular Weights:

$CaCO_3$	$MgCO_3$	CaO	MgO	CO_2
100.1	84.32	56.08	40.32	44.0

Example 4.1 - Stoichiometry

Basis: 100 lbm of limestone

Component i	Mass (lbm)	MW (lbm/lbmol)	Mole (lbmol)
$CaCO_3$	92.89	100.1	0.9280
$MgCO_3$	5.42	84.32	0.0642
Inerts	1.70	- - -	- - -
Total	**100.0**		- - -

Example 4.1 - Stoichiometry

Calculate the amount of products formed:

$$0.9280\,\text{lbmol CaCO}_3\left(\frac{1\,\text{lbmol CaO}}{1\,\text{lbmol CaCO}_3}\right)\left(\frac{56.08\,\text{lbm CaO}}{1\,\text{lbmol CaO}}\right)=52.04\,\text{lbm CaO}$$

$$0.0642\,\text{lbmol MgCO}_3\left(\frac{1\,\text{lbmol MgO}}{1\,\text{lbmol MgCO}_3}\right)\left(\frac{40.32\,\text{lbm MgO}}{1\,\text{lbmol MgO}}\right)=2.59\,\text{lbm MgO}$$

$$0.9280\,\text{lbmol CaCO}_3\left(\frac{1\,\text{lbmol CO}_2}{1\,\text{lbmol CaCO}_3}\right)\left(\frac{44.0\,\text{lbm CO}_2}{1\,\text{lbmol CO}_2}\right)=40.83\,\text{lbm CO}_2$$

$$0.0642\,\text{lbmol MgCO}_3\left(\frac{1\,\text{lbmol CO}_2}{1\,\text{lbmol MgCO}_3}\right)\left(\frac{44.0\,\text{lbm CO}_2}{1\,\text{lbmol CO}_2}\right)=2.82\,\text{lbm CO}_2$$

Example 4.1 - Stoichiometry

Summary of Products

Source	Lime		CO_2 (lbm)
	Component	Mass (lbm)	
$CaCO_3$	CaO	52.04	40.83
$MgCO_3$	MgO	2.59	2.82
Inerts	Inerts	1.70	- - -
Total		56.33	43.65

Example 4.1 - Stoichiometry

Solution for (a):

$$m_{CaO} = 5\,\text{tons stone}\left(\frac{2000\,\text{lbm}}{1\,\text{ton}}\right)\left(\frac{52.04\,\text{lime}}{100\,\text{lbm stone}}\right) = 5200\,\text{lbm CaO}$$

Solution for (b):

$$\text{Ratio} = \frac{43.65\,CO_2}{100\,\text{lbm stone}} = 0.437\,\frac{\text{lbm}\,CO_2}{\text{lbm stone}}$$

Solution for (c):

$$m_{stone} = 1\,\text{ton lime}\left(\frac{2000\,\text{lbm}}{1\,\text{ton}}\right)\left(\frac{100\,\text{lbm stone}}{56.33\,\text{lbm lime}}\right) = 3550\,\text{lbm stone}$$

Limiting and Excess Reactants

Limiting Reactant

The reactant that is present in the smallest stoichiometric amount. It is the compound that will be consumed first if the reaction proceeds to completion.

Excess Reactant

The chemical species whose amount supplied is higher than the stoichiometric requirement. The percentage excess is then computed as:

$$\%\text{Excess} = \frac{(\text{actual amount present - theoretical amount needed})}{\text{theoretical amount needed}} \times 100$$

Limiting and Excess Reactants

Consider a balanced chemical reaction:

$$\mathbf{aA + bB \Longrightarrow cC + dD}$$

Suppose x moles of A and y moles of B are present and they react according to the above reaction,

$$\text{if } \left(\frac{x}{y}\right) < \left(\frac{a}{b}\right) \text{ then reactant A is limiting}$$

$$\text{if } \left(\frac{x}{y}\right) > \left(\frac{a}{b}\right) \text{ then reactant B is limiting}$$

Conversion and Degree of Completion

Conversion
The fraction (or percentage) of the reactants that actually reacted during the reaction.

$$\%\text{Conversion} = \frac{\text{amount of reactant converted}}{\text{amount of reactant supplied}} \times 100$$

Degree of Completion
The fraction (or percentage) of the limiting reactant converted into products.

$$\text{Degree of Completion} = \frac{\text{amount of lim. reactant converted}}{\text{amount of lim. reactant supplied}} \times 100$$

Yield and Selectivity

Yield

The actual amount of products formed relative to what is actually expected from the reaction.

$$\%\text{Yield} = \frac{\text{actual amount of product formed}}{\text{theoretical amount of product expected}} \times 100$$

Selectivity

The ratio of the moles of the desired product produced to the moles of undesired product (by-product).

$$\text{Selectivity} = \frac{\text{moles of desired product formed}}{\text{moles of undesired product formed}}$$

Yield and Selectivity

For example, methanol (CH_3OH) can be converted into ethylene (C_2H_4) and propylene (C_3H_6) by the reaction:

$$\mathbf{2\,CH_3OH \Longleftrightarrow C_2H_4 + 2\,H_2O}$$

$$\mathbf{3\,CH_3OH \Longleftrightarrow C_3H_6 + 3\,H_2O}$$

If the desired product is ethylene, then the selectivity is computed as:

$$\text{Selectivity} = \frac{\text{moles of ethylene formed}}{\text{moles of propylene formed}}$$

Example 4.2 – Chemical Equation and Stoichiometry

Antimony (Sb) 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

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

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. Determine:

a. The limiting reactant
b. The percentage of the excess reactant
c. The degree of completion (fraction)
d. The percent conversion of stibnite
e. The mass yield relative to stibnite supplied

Example 4.2 – Chemical Equation and Stoichiometry

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

Component	kg	Mol. Wt.	gmol
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	- - -

Example 4.2 – Chemical Equation and Stoichiometry

Solution for (a):

From chemical equation:

$$\left(\frac{\text{mol}\,Sb_2S_3}{\text{mol}\,Fe}\right)_{\text{stoichiometric}} = \frac{1}{3} = 0.33$$

Based on the actual supply:

$$\left(\frac{\text{mol}\,Sb_2S_3}{\text{mol}\,Fe}\right)_{\text{actual}} = \frac{1.77}{4.48} = 0.40$$

Since actual ration > stoichiometric ratio, hence, Fe is the limiting reactant and Sb_2S_3 is the excess reactant.

Example 4.2 – Chemical Equation and Stoichiometry

Solution for (b):

The Sb2S3 required to react with the limiting reactant is

$$4.48\,\text{gmol Fe}\left(\frac{1\,\text{gmol}\,Sb_2S_3}{3\,\text{gmol Fe}}\right)=1.49\,\text{gmol}\,Sb_2S_3$$

The percentage of excess reactant is

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

Example 4.2 – Chemical Equation and Stoichiometry

Solution for (c):

Determine how much Fe actually does react:

$$1.64\,\text{gmol Sb}\left(\frac{3\,\text{gmol Fe}}{2\,\text{gmol Sb}}\right) = 2.46\,\text{gmol Fe}$$

The fractional degree of completion is

$$\text{fractional deg. of completion} = \frac{2.46\,\text{gmol Fe}}{4.48\,\text{gmol Fe}} = 0.55$$

Example 4.2 – Chemical Equation and Stoichiometry

Solution for (d):

Determine how much Sb_2S_3 actually does react:

$$1.64\,\text{gmol Sb}\left(\frac{1\,\text{gmol}\,Sb_2S_3}{2\,\text{gmol Sb}}\right)=0.82\,\text{gmol}\,Sb_2S_3$$

The percentage conversion is

$$\%\text{conversion } Sb_2S_3 = \frac{0.82\,\text{gmol}\,Sb_2S_3}{1.77\,\text{gmol}\,Sb_2S_3}\times 100 = 46.3\%$$

Example 4.2 – Chemical Equation and Stoichiometry

Solution for (e):

As required, the yield is expressed in terms of the mass of product (Sb) formed per mass of stibnite fed.

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

Extent of Reaction (ε)

The extent of the reaction (ξ) is an extensive quantity describing the progress of a chemical reaction. Depends on the degree of completion of the reaction

$$\mathbf{N_i = N_{i0} \pm v_i \varepsilon}$$

where N_i = molar amount remaining of species I

N_{i0} = initial amount in the feed

v_i = stochiomettric coefficient
(+ for product, – for reactants)

ε = extent of reaction

Equilibrium Constant, K

Consider a reversible chemical reaction,

$$\mathbf{aA + bB \;<\!\!=\!=\!=\!=\!=\!=\!>\; cC + dD}$$

At equilibrium,

There will be no net change in the amount of each chemical species. Hence, their individual concentrations are already constant. The equilibrium constant can be defined by,

$$k = \frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{P_C^c P_D^d}{P_A^a P_B^b} = \frac{y_C^c y_D^d}{y_A^a y_B^b}$$

Example 4.3 – Chemical Equation and Stoichiometry

The gas-phase reaction between methanol and acetic acid to form methyl acetate and water takes place in a batch reactor and proceeds to equilibrium.

$$\underset{(A)}{CH_3OH} + \underset{(B)}{CH_3COOH} \Longleftrightarrow \underset{(C)}{CH_3COOCH_3} + \underset{(D)}{H_2O}$$

When the reaction mixture comes to equilibrium, the mole fractions (y) of the four reactive species satisfy the relation

$$\frac{y_C y_D}{y_A y_B} = 4.87$$

Example 4.3 – Chemical Equation and Stoichiometry

a. If the feed to the reactor contains equimolar quantities of methanol and acetic acid and no other species, calculate the fractional conversion at equilibrium.

b. It is desired to produce 70 mol of methyl acetate starting with 80 mol acetic acid. If the reaction proceeds to equilibrium, how much methanol must be fed? Assume no products are present initially.

c. What is the composition of the final mixture at equilibrium in terms of the mole fractions?

Example 4.3 – Chemical Equation and Stoichiometry

Solution to (a):

Let n_A, n_B, n_C, and n_D be the respective molar quantities of A, B, C, and D at equilibrium. The total moles (n_T) is

$$\mathbf{n_T = n_A + n_B + n_C + n_D}$$

Expressing the equilibrium amounts in terms of initial amounts using the extent of reaction.

$$\mathbf{n_A = n_{A0} - (1)\varepsilon}$$
$$\mathbf{n_B = n_{B0} - (1)\varepsilon}$$
$$\mathbf{n_C = n_{C0} + (1)\varepsilon}$$
$$\mathbf{n_D = n_{D0} + (1)\varepsilon}$$

Example 4.3 – Chemical Equation and Stoichiometry

The mole fractions at equilibrium are

$$y_A = n_A/n_T = (n_{A0} - \varepsilon)/n_T$$

$$y_B = n_B/n_T = (n_{B0} - \varepsilon)/n_T$$

$$y_C = n_C/n_T = (n_{C0} + \varepsilon)/n_T$$

$$y_D = n_D/n_T = (n_{D0} + \varepsilon)/n_T$$

And the equilibrium constant can be written as

$$\frac{(n_{C0} + \varepsilon)(n_{D0} + \varepsilon)}{(n_{A0} - \varepsilon)(n_{B0} - \varepsilon)} = 4.87$$

Example 4.3 – Chemical Equation and Stoichiometry

For a basis of 1 gmol of A (initial amount)

$$\mathbf{n_{A0} = n_{B0} = 1\ gmol}$$
$$\mathbf{n_{C0} = n_{D0} = 0}$$

Using these values in the equilibrium constant relation:

$$\frac{(\varepsilon)(\varepsilon)}{(1-\varepsilon)(1-\varepsilon)} = \mathbf{4.87}$$

Rearranging the equation:

$$\mathbf{3.87\varepsilon^2 - 9.74\varepsilon + 4.87 = 0}$$

Example 4.3 – Chemical Equation and Stoichiometry

Solving for ε:

$$\boldsymbol{\varepsilon_1 = 1.83\ \text{gmol and}\ \varepsilon_2 = 0.688\ \text{gmol}}$$

The last value is chosen since the first one results to a negative conversion. Solving for fractional conversion:

$$X_A = \frac{\text{amount of A reacted}}{\text{initial amount of A}} = \frac{N_A - N_{A0}}{N_{A0}} = \frac{\varepsilon}{N_{A0}}$$

$$X_A = \frac{0.688\,\text{gmol}}{1\,\text{gmol}} = 0.688$$

Example 4.3 – Chemical Equation and Stoichiometry

Solution to (b):

The initial amounts of the components are

$$\mathbf{n_{A0} = \text{to be calculated and } n_{B0} = 80 \text{ gmol}}$$
$$\mathbf{n_{C0} = n_{D0} = 0}$$

And the amounts at equilibrium are

$$(1)\ \mathbf{n_A = n_{A0} - \varepsilon = n_{A0} - \varepsilon}$$
$$(2)\ \mathbf{n_B = n_{B0} - \varepsilon = (80 \text{ gmol}) - \varepsilon}$$
$$(3)\ \mathbf{n_C = n_{C0} + \varepsilon = (0) + \varepsilon = 70 \text{ gmol}}$$
$$(4)\ \mathbf{n_D = n_{D0} + \varepsilon = (0) + \varepsilon}$$

Example 4.3 – Chemical Equation and Stoichiometry

From (3), ε = 70 gmol

Updating the set of equations

(1) $\mathbf{n_A = n_{A0} - 70}$
(2) $\mathbf{n_B = 80 - 70 = 10\ gmol}$
(3) $\mathbf{n_C = \varepsilon = 70\ gmol}$
(4) $\mathbf{n_D = \varepsilon = 70\ gmol}$

Writing the equilibrium constant relation:

$$\frac{n_C n_D}{n_A n_B} = \frac{(70\,\text{gmol})(70\,\text{gmol})}{(n_{A0} - 70\,\text{gmol})(10\,\text{gmol})} = 4.87$$

Example 4.3 – Chemical Equation and Stoichiometry

Solving the last equation for n_{A0}:

$$\mathbf{n_{A0} = 170.6\ gmol\ of\ methanol}$$

Solution for (c):

Component	Moles at equilibrium	Mole Fraction
A	n_A = 100.6 gmol	y_A = 0.401
B	n_B = 10 gmol	y_B = 0.040
C	n_C = 70 gmol	y_C = 0.279
D	n_D = 70 gmol	y_D = 0.279
Total	**n_T = 250.6 gmol**	**1.000**