Multiple Reactions

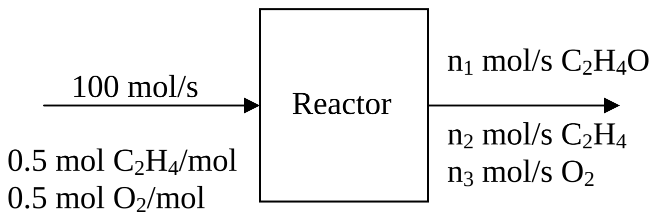
We will define several terms that are used in material balance calculations when chemical reactions are involved.

100 mol/s of equimolar mixture containing ethylene and oxygen is fed to a reactor where they combine to make ethylene oxide. The fractional conversion of ethylene is 20%. Find flow rates of all components in reactor exit stream at steady state.

First write balanced chemical equation

$$2C_2H_4 \quad + \quad O_2 \longrightarrow C_2H_4O$$

Then, draw a flowchart and label inlet and exit streams of the reactor.



If ethylene and oxygen are supplied to the reactor in the mole ratio of 2, we say that they are fed in stoichiometric ratio (see the equation above) and they are in stoichiometric quantities. The reactant present in less than stoichiometric quantity is called limiting reactant. In the above example, oxygen is the limiting reactant because its stoichiometric quantity is 100 moles of oxygen.

$$\text{Fractional conversion, } f = \frac{\text{Moles reacted}}{\text{Moles fed}}$$

We define extent of reaction as number of moles reacted and use the symbol ξ for it.

Write balance of C_2H_4: in – out + ~~generation~~ – consumption = ~~accumulation~~

Why have generation and accumulation terms been canceled?

$$50 \text{ (mol/s)} - n_2 \text{ (mol/s)} - \xi \text{ (mol/s)} = 0$$

ξ is number of moles of ethylene reacted. In this problem,

$$\xi = 0.2 \times 50 \text{ mol/s} = 10 \text{ mol/s}$$

Therefore, n_2 = 40 mol/s.

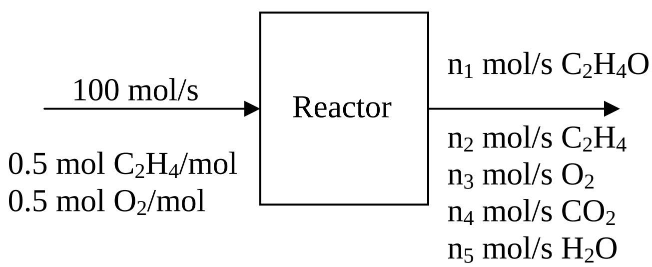
Balance of oxygen: 50 mol/s – n_3 mol/s – $\xi/2$ mol/s = 0 or n_3 = 45 mol/s.

You could write balance of C_2H_4O also.

Now, in the same reactor an additional reaction in which C_2H_4 could combine with O_2 to produce CO_2 and H_2O can also occur. This reaction is side reaction and the products of this reaction are undesired products. C_2H_4O is the desired product.

$$C_2H_4 + 3O_2 \longrightarrow CO_2 + H_2O \quad \text{side reaction}$$

If fractional conversion remains same at 20%, we want to find molar flow rates of components in exit stream. Draw a flowchart and label the streams.



ξ_1 = extent of reaction in reaction producing C_2H_4O
ξ_2 = extent of reaction in reaction producing CO_2

$$f = \frac{\xi_1+\xi_2}{50} = 0.2 \text{ or } \xi_1+\xi_2 = 10 \text{ mol/s}$$

You could write balances of all species involved and organize it in the following way

Species	balance equation
C_2H_4	$50 - n_2 - \xi_1 - \xi_2 = 0$
C_2H_4O	$- n_1 + \xi_1 = 0$
O_2	$50 - n_3 - \xi_1/2 - 3\xi_2 = 0$
CO_2	$- n_4 + 2\xi_2 = 0$
H_2O	$- n_5 + 2\xi_2 = 0$

C_2H_4O is the desired product and CO_2 is undesired. Obviously, we want to produce more of the former than the latter. To quantify, the relative production rates of desired and undesired products, we define

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

Suppose selectivity = 4.5 in the above problem, then $\dfrac{\xi_1}{2\xi_2} = 4.5$ or $\xi_1 = 9\xi_2$

Combine fractional conversion and selectivity to find ξ_1 and ξ_2 and then the molar flow rates of all species.

Yield is another term that signifies the amount of desired product made:

$$\text{Yield} = \frac{\text{Moles of desired product}}{\text{Moles of desired product made if the limiting reacting reacts completely}}$$

Yield of C_2H_4O in the above problem = $\xi_1/50 = 0.18$ (*check!* why is 50 used in the denominator?)

What we did so far is balances of molecular species like C_2H_4, C_2H_4O, CO_2, H_2O and O_2.

Atomic species balance, that is balance of atomic C, atomic H and atomic O, could also be done.

For atomic species, input = output because atoms can neither be generated nor destroyed.

For the above problem,

Balance of atomic C: 50 mol/s C_2H_4 x 2 mol C/1 mol $C_2H_4 = 2n_1 + 2n_2 + n_4$

Balance of atomic H: 50 mol/s x 4 mol H/1 mol $C_2H_4 = 4n_1 + 4n_2 + 2n_5$

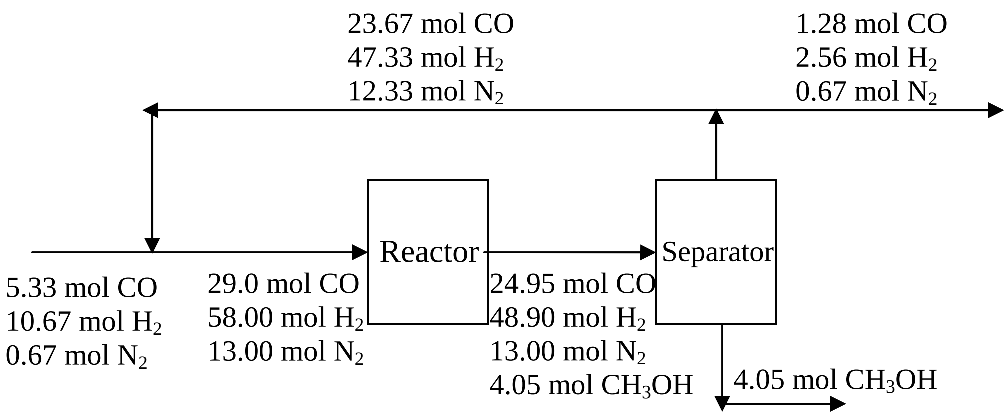
Balance of atomic O: 50 mol/s x 2 mol O/1mol $O_2 = n_1 + 2n_3 + 2n_4 + n_5$

Two more equations, one for selectivity and one for fractional conversion, could be written and all unknowns could be solved for.

You will find that making atomic balances simplifies the analysis of material balance calculations (recall the problem on purge solved in the tutorials)

Purge

If an inert material (which does not react) is present in a mixture of materials being fed to a reactor and the unreacted reactants are separated and recycled to the reactor, a part of the recycle stream is purged to prevent accumulation of the inert material in the process. Consider the following flowchart of a process with recycle and purge



Methanol is made by reacting carbon dioxide and hydrogen. The fresh feed to the process contains 0.67 mol of N_2, which is an inert material because it does not react. Hence, it should be purged or bled from the recycle stream. If feed to the process does not contain N_2, there is no need for purge.

Conversions

$$\text{Single pass conversion} = \frac{\text{Reactant input to the reactor} - \text{Reactant output to the reactor}}{\text{Reactant input to the reactor}}$$

$$\text{Overall conversion} = \frac{\text{Reactant input to the process} - \text{Reactant output to the process}}{\text{Reactant input to the process}}$$

For the above flowchart,

$$\text{single pass conversion of CO} = \frac{29.00 \text{ mol CO} - 24.95 \text{ mol CO}}{29.00 \text{ mol CO}} = 14\%$$

$$\text{Overall conversion of CO} = \frac{10.67 \text{ mol CO} - 1.28 \text{ mol CO}}{10.67 \text{ mol CO}} = 88\%$$

Combustion reactions

These reactions involve burning fuel (solid, liquid and gas) with oxygen (or specifically air). Heat is generated because the reactions are exothermic. This heat is utilized in producing steam, which in turn drives turbines to generate electricity. Many power intensive chemical industries such as cement have captive power plants to ensure continuous supply of power.

Liquid fuels generally used in industry are heavy petroleum fractions and gaseous fuels are natural gas (mostly methane), hydrogen, ethane, propane, butane etc.

When carbon in fuels is converted to only carbon dioxide, we call the process as complete combustion; if CO is also produced, the process is partial combustion. Hydrogen is converted to water and sulphur is converted to sulphur dioxide.

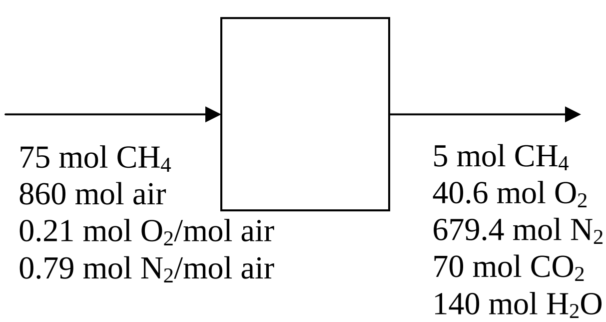
Air (or oxygen) is supplied in more than stoichiometric quantities to make sure that all of the fuel fed to a combustion chamber reacts. In other words, the fuel is the limiting reactant. The following definitions are useful in combustion reactions:

Theoretical oxygen: amount of oxygen required for 100% conversion of fuel to carbon dioxide.

Theoretical air: amount of air corresponding to theoretical oxygen.

$$\text{Excess air} = \frac{\text{Moles air fed} - \text{Theoretical moles of air}}{\text{Moles air fed}}$$

Consider the following combustion process in which methane is burned. Find excess air.



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

Theoretical oxygen = 150 moles even though only 140 moles of O_2 are consumed for 70 mol of CH_4 reacted. Keep this is mind whenever you make excess and theoretical air calculations.

Oxygen supplied = 180.6 moles

$$\text{Excess oxygen} = \frac{180.6 - 150}{180.6} = 16.95\%$$

In the above process, even if some of the methane burns to produce CO, excess air and theoretical air will remain same. Excess and theoretical air or oxygen are always based on 100% conversion of fuel to CO_2.

Sometimes, the composition of product gases of combustion is reported on a dry basis. This means that the composition does not take into account the amount of water present in the gas. Wet basis includes water. A gas containing 40% CH_4 and 40% H_2 and 20% H_2O on a wet basis would contain 50% CH_4 and 50% H_2 on a dry basis.

Test Your Understanding

1. Explain in your own words the meaning of purge
2. Check atomic species balance over the reactor and for the entire process in the problem described in this handout where ethylene combines with oxygen to produce ethylene oxide
3. In the problem on excess air, what is excess air if 2% of methane burned forms CO?
4. In the problem on excess air, what is excess air if conversion of methane is 90%?
5. What are single pass and overall conversions?
6. In the problem described in **Purge** section, what are single and overall conversions, if 5 moles of methanol are formed and 2 moles of CO are purged?
7. A gas contains 1 mole of H_2, 1 mol of O_2, 3 mol of C_2H_4, 6 mol CO_2 and 6 mol of H_2O. What is the molar composition of this gas on a wet basis? On a dry basis?