Consistency of Atomic and Molecular Balances in Describing Chemical Reaction

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last updated: August 17, 2011 ~~May 28, 2009~~

Consider a furnace in which a fuel (F), methane, is burned in air (A) to produce heat and a stack (S) gas, as shown in Figure 1. You are given the composition and flowrate of the air and and the fuel stream. In what was likely your first course in the chemical engineering department, you learned that you could describe the steady state operation of this system with an atom balance <u>if and only if</u> you were given a few key pieces of information. Typically, that information was given as the statement, "Assume complete combustion."

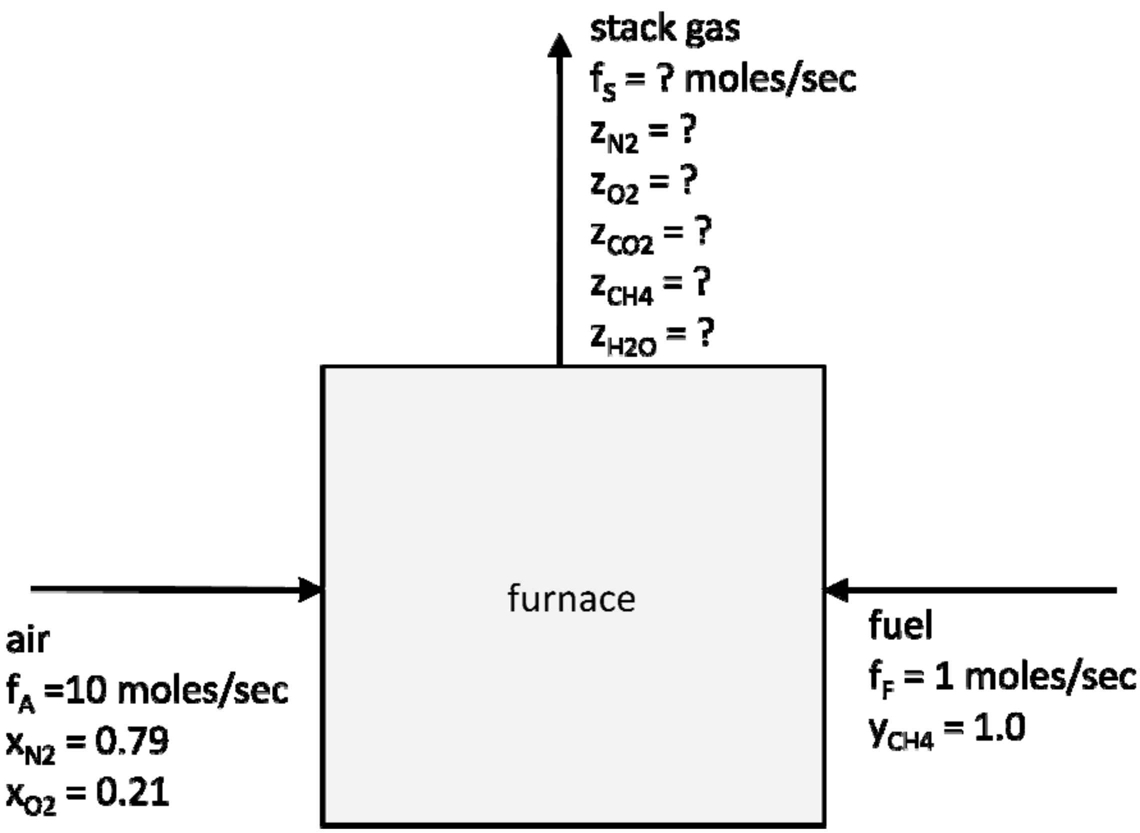

Figure 1. A furnace burning methane in air.

The assumption of complete combustion first gave you a chemical reaction, namely

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (1)$$

The assumption of complete combustion eliminated the possibility of other reactions taking place, such as

$CH_4 + 3/2O_2 \rightarrow CO + 2H_2O$ (2)

The assumption of complete combustion also told you that all of the methane was burned. This information can be interpreted in two ways. First, we know that the mole fraction of methane in the stack gas is zero, $z_{CH4} = 0$. Second, based on the stoichiometry of the reaction in equation (1), we know that for every molecule of methane to converted to carbon dioxide, two molecules of oxygen were consumed and two molecules of water were produced.

We see that molecules of a species are not conserved in the presence of a reaction but the number of each type of atom is. Therefore, we chose to write atom balances to describe this process. We start with the generic balance

accumulation = in – out + generation (3)

At steady state, there is no accumulation. If we write this balance for atoms, there is no generation and we simply have,

in = out (4)

For each atom, we can write

$$f_A\left(\sum_{i}^{species} u_{i,j}x_i\right) + f_F\left(\sum_{i}^{species} u_{i,j}y_i\right) = f_S\left(\sum_{i}^{species} u_{i,j}z_i\right) \quad (5)$$

where $u_{i,j}$ is the number of atoms of type j in a molecule of type i. Note that $u_{i,j}$ is zero if atom j is not in molecule i. For the problem at hand we can write the u matrix in Table 1.

	N_2	O_2	CH_4	CO_2	H_2O
N	2	0	0	0	0
O	0	2	0	2	1
C	0	0	1	1	0
H	0	0	4	0	2

Table 1. Atomic stoichiometric coefficient matrix.

For each atom type we then have,

$$\begin{aligned} f_A(2x_{N2}) &= f_S(2z_{N2}) \\ f_A(2x_{O2}) &= f_S(2z_{CO2} + z_{H2O}) \\ f_F(y_{CH4}) &= f_S(z_{CO2}) \\ f_F(4y_{CH4}) &= f_S(2z_{H2O}) \end{aligned} \quad (6)$$

These four atom balances, along with the fact that the sum of the mole fractions in the stack gas is unity,

$$z_{CO2} + z_{H2O} + z_{CO2} + z_{N2} = 1 \quad (7)$$

provide five equations, which can be solved for five unknowns. If instead of 100% conversion of methane to carbon dioxide, we were told we had χ% conversion, then we would have one more unknown, since z_{CH4} was no longer zero, the atom balance on carbon would change to

$$f_F(y_{CH4}) = f_S(z_{CO2} + z_{CH4})$$

and we would require one more equation that related conversion to the flowrates and mole fractions.

In general, conversion is defined in terms of a limiting reagent. The limiting reagent is the species most limits how far the reaction can proceed. In our example, we have $f_F(y_{CH4}) = 1.0\ moles/sec$ of methane and $f_A(x_{O2}) = 2.1\ moles/sec$ of molecular oxygen. Based on the stoichiometric coefficients of the reaction given in equation (1), we require 2 moles of molecular oxygen per mole of methane. Since we are inputting more than 2 moles of molecular oxygen per mole of methane, methane is the limiting reagent. If we want a methodical procedure for determining the limiting reagent for a system with a single reaction, then we should calculate the moles in of each reactant divided by the absolute value of the stoichiometric coefficient. The species with the smallest value is the limiting reagent,

$$\min\left(\frac{moles\ in\ of\ reactant\ i}{|\nu_i|}\right)$$

We use the absolute value of the stoichiometric coefficient because we assume that coefficients of reactants are negative and coefficients of products are positive. In this example, our numbers would be 1.0 moles/sec for methane and 1.05 moles/sec of molecular oxygen. Since the number is smaller for methane, methane is the limiting reagent.

Having identified the limiting reagent, we can define conversion as

$$\chi \equiv \frac{moles\ of\ limiting\ reagent\ reacted}{moles\ of\ limiting\ reagent\ provided}$$

or, alternatively we can define the conversion through how much went unreacted

$$1\text{-}\chi \equiv \frac{moles\ of\ limiting\ reagent\ unreacted}{moles\ of\ limiting\ reagent\ provided}$$

For this example, the moles of methane unreacted is $f_S z_{CH4}$ and the moles of methane provided is $f_F y_{CH4}$ so the conversion is given by

$$1 - \chi = \frac{f_S z_{CH4}}{f_F y_{CH4}} \tag{8}$$

Equation (8) is a statement about the extent of reaction, or conversion, in the furnace. We will see that the concept of conversion is very common in chemical reaction engineering. If we have 100% conversion (χ=1), we see that this dictates that $z_{CH4} = 0$ and we return to the original problem. Otherwise, we have six equations for six unknowns, which we can solve.

This combustion problem can also be solved using balances on the molecules. In this case, equation (3) becomes at steady state

$$0 = \text{in} - \text{out} + \text{generation} \tag{9}$$

The generation term cannot be ignored since molecular species are consumed and produced by the chemical reaction. The generation term can be written as a function of the moles of limiting reagent (l.r.) reacted. Rearrangement of the definition of the conversion given above yields

$$moles\ of\ l.r.reacted = \chi(moles\ of\ l.r.provided)$$

We must account for the fact that all species participating in the reaction are consumed or generated at the same rate, as indicated by the stoichiometric coefficient. The amount of species i consumed or generated by the reaction can be related to the amount of the limiting reagent consumed by the reaction as

$$moles\ of\ i\ reacted = \frac{v_i}{|v_{l.r.}|}(moles\ of\ l.r.reacted)$$

where the sign of the stoichiometric coefficient of species *i* will determine if species i is consumed (negative) or produced (positive) in the reaction.

For our particular example, the limiting reagent is methane and the moles of l.r. reacted is

$$moles\ of\ l.r.reacted = \chi f_F y_{CH4}$$

Therefore, we can write a balance on each molecular species as

$$0 = f_A x_i + f_F y_i - f_S z_i + \frac{v_i}{|v_{CH4}|}\chi f_F y_{CH4} \tag{10}$$

where v_i is the stoichiometric coefficient of molecule *i* in the reaction given in equation (1). Note again that the stoichiometric coefficient is negative for products and positive for reactants and zero for components not involved in the reaction. The values of the stoichiometric coefficients for the reaction in equation (1) are given in Table 2. Thus the generation term is negative for products and positive for reactants. The generation term simply states that the amount of material consumed/produced of a given molecular species is proportional to the amount of methane consumed where the proportionality constant is the ratio of the stoichiometric coefficients and the amount of methane consumed is simply χ times the amount of methane fed into the reactor, $f_F y_{CH4}$. Methane is singled out here only because it is the species upon which the conversion was based.

	N_2	O_2	CH_4	CO_2	H_2O
reaction 1	0	-2	-1	1	2

Table 2. Reaction stoichiometric coefficient matrix.

For each molecular species, we then have

$$0 = f_A x_{N2} - f_S z_{N2}$$

$$
\begin{aligned}
0 &= f_A x_{O2} - f_S z_{O2} - 2\chi f_F y_{CH4} \\
0 &= f_F y_{CH4} - f_S z_{CH4} - \chi f_F y_{CH4} \\
0 &= -f_S z_{CO2} + \chi f_F y_{CH4} \\
0 &= -f_S z_{H2O} + 2\chi f_F y_{CH4}
\end{aligned}
\tag{11}
$$

Equation (11) along with the fact that the sum of the mole fractions is zero gives six equations for six unknowns. Examination of the methane balance shows that it is equivalent to equation (8), upon which we based our conversion information. So even in the solution of the system based on atomic balances, we had to have some input from a molecular balance.

The actual numerical solution of either the system of atomic balances or molecular balances is left as a student exercise.

This demonstration serves three purposes.

- First it shows that there is an equivalence between a solution based on atomic balances and one based on molecular balances, as of course there must be.
- Second, it shows the importance of developing some concept of an extent of a reaction or conversion.
- Third, it illustrates the fact that in order to solve this problem, we have to be given the conversion, χ. Where did that number come from? It was given to us in the problem statement, but in real life, someone had to calculate it. As part of this course in Reaction Engineering Fundamentals, we will develop the theory required to determine the conversion of a reaction as a function of the type of reactor and the operating conditions.