STOICHIOMETRY: A Tool in Gas Appliance Development

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Stoichiometry is the study of volume, mass, and energy relationships in chemical reactions. In gas appliance engineering, this means the combustion reactions between fuel gas and air. It is here greatly simplified since all reactions are in the gaseous state and at pressures and temperatures where the conventional gas laws apply within limits of accuracy sufficient for daily use. The following six principles cover the needs of the domestic gas appliance field:

1. A molecule of any gas occupies the same volume as a molecule of any other gas. Put another way, the molecular weight of any gas, expressed in pounds, will occupy the same volume as that of any other gas. At standard conditions of 32 °F and 29.92 in mercury column pressure, this is 559 cu ft. Thus 32 lb of O₂, or 2.616 lb of H₂, or 44.0 lb of CO₂ will occupy 350 cu ft. The actual number of cubic feet is not the important thing; rather the fact that, in a chemical equation involving gases, each symbol represents a definite volume. For example, the equation:

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]

not only describes the chemistry of burning methane and oxygen, but also says that 1 cu ft of methane burns with 2 cu ft of oxygen to produce 1 cu ft of carbon dioxide and 2 cu ft of water vapor.

2. In a mixture of gases, each gas occupies its own volume. A mixture of 20.92 cu ft of O₂, 78.14 cu ft of N₂, and 0.94 cu ft of odds and ends will occupy:

\[ 20.92 + 78.14 + 0.94 = 100.0 \text{ cu ft} \]

(This mixture is called dry air.)

3. In a mixture of gases of different specific gravities (air is referred to as 1.00), the specific gravity of the mixture is the weighted average of the individual gases. For example, in a mixture of 90\% methane (sp gr = .5455) and 10\% ethane (sp gr = 1.0493) by volume, the sp gr of the mixture is:

\[ (.90 \times .5455) + (.10 \times 1.0493) = .59588 \]

incidentally, since the average molecular weight of air is 28.37 (which may be rounded off to 29.0), the specific gravity of any other gas can be obtained by
dividing its molecular weight by 29.0. For example the specific gravity of butane, \(C_4H_{10}\), molecular weight 58.08, is \(58.08/29.0 = 2.00\)

4. When a mixture of combustible gases burns, each delivers its own amount of energy, regardless of what others may be present. For example, in burning a cubic foot of gas which by volume is 90% methane, at 1014 Btu/cu ft, and 10% ethane at 1780 Btu/cu ft, the amount of heat given off is:

\[0.9 \times 1014 + 0.1 \times 1780 - 1690.6 \text{ Btu/cu ft}\]

5. If a given volume of gas is heated a given amount while being allowed to expand at constant pressure, a certain amount of heat is required. When it cools back to its original temperature, the same amount of heat is given off. This is not as simple a relationship as those above, since the amount of heat (known as the "specific heat at constant pressure") or \(C_p\) varies with the individual gas and with the starting temperature. This is available in any set of reference tables. Fig 1 puts it in a convenient form for gas appliance work.

6. The volume of a gas is proportional to the absolute temperature (degrees \(F + 460\)) and inversely proportional to the absolute pressure.

One of the best examples of application of stoichiometric principles is the computation of fuel loss as it was done before the availability of the alignment charts. Five of the above six principles are used. For that reason, it is worthwhile going through such a computation in detail to show how these principles may be applied.

First, the fuel gas analysis must be known. This is usually available from the gas company. For a typical natural gas, the constituents of 1 cu ft are:

- CH\(_4\) 0.22
- C\(_2\)H\(_6\) 0.098
- CO\(_2\) 0.014
- O\(_2\) 0.002
- N\(_2\) 0.012

Next, the combustion reactions involved are written:

\[
\text{CH}_4 + 2\text{CO}_2 \rightarrow \text{CO}_2 + 3\text{H}_2\text{O} \\
\text{C}_2\text{H}_6 + 3\frac{1}{2}\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}
\]

Using the above, prepare a table showing the volume of products and the O\(_2\) requirement for theoretical combustion of 1 cu ft of the gas. Include combustion air require-
ment on the basis that for each 0.209 cu ft of O\(_2\), it will be necessary to provide 1.0 cu ft of air; and compute N\(_2\) (including inert) on the basis that for each 0.209 cu ft of O\(_2\) there will be 0.791 cu ft of N\(_2\).

Tabulate the heating value of the individual constituents and (although not required in the computations) the specific gravities:

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Partial Volume</th>
<th>CO(_2)</th>
<th>(\text{H}_2\text{O})</th>
<th>O(_2)</th>
<th>N(_2)</th>
<th>Air</th>
<th>Sp Gr.</th>
<th>Heating Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>.882</td>
<td>.882</td>
<td>1.764</td>
<td>1.764</td>
<td>6.68</td>
<td>8.44</td>
<td>.481</td>
<td>894.8</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>.098</td>
<td>.196</td>
<td>.294</td>
<td>.343</td>
<td>1.36</td>
<td>1.64</td>
<td>.103</td>
<td>174.4</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>.014</td>
<td>.014</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.021</td>
</tr>
<tr>
<td>O(_2)</td>
<td>.002</td>
<td></td>
<td>-.002</td>
<td>-.01</td>
<td>-.01</td>
<td></td>
<td>.002</td>
<td></td>
</tr>
<tr>
<td>N(_2)</td>
<td>.012</td>
<td></td>
<td></td>
<td></td>
<td>.01</td>
<td></td>
<td>.011</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>1.092</td>
<td>2.058</td>
<td>2.105</td>
<td>7.98</td>
<td>10.07</td>
<td>.618</td>
<td>1069.2</td>
</tr>
</tbody>
</table>

From this table, derive the following additional factors which will be used in the computation:

\[
\text{Volume Dry Products (VDP)} = \text{the sum of the CO}_2 \text{ and N}_2 \text{ in the combustion products of 1 cu ft of gas. In this case}
\]

\[
\text{VDP} = 1.092 + 7.98 = 9.07 \text{ cu ft}
\]

Air Required (AR) = 10.07 cu ft

Ultimate CO\(_2\) (ULT) which equals the volume percent CO\(_2\) in the dry products, or

\[
\text{ULT} = \frac{1.092}{9.07} = 12.06\%
\]

At this point may be interpolated the reason for using dry products in volume computations. Great analysis, as is regularly used in working with combustion products, has the effect of cancelling out the volume of water vapor due to condensation, so all calculations are on a "dry" basis (although the gases being analyzed are actually saturated with water vapor). However, the specific heat and the latent heat of the water vapor are not overlooked in the energy computations.

The above table represents theoretical combustion with no excess air. In practice, considerable excess air is present and carries a considerable part of the heat lost up the flue. The volume of excess air per cubic foot of gas burned will be represented by the symbol
XS. By adding this to VDP, a new quantity is obtained: volume of total dry products (VTDP) including XS produced by combustion of one cubic foot of gas.

It is obvious that, as theoretical combustion products are diluted with excess air, the observed (Orsat) CO₂ will drop below ULT proportionately.

The relationship is:

\[
\text{VTDP} = \text{VDP} - \frac{\text{ULT}}{\text{Obs'd CO}_2} \text{ cu ft}
\]

Since \( X_S = \text{VTDP} - \text{VDP} \), substituting in the above produces:

\[
X_S = \text{VDP} \times \left( \frac{\text{ULT}}{\text{Obs'd CO}_2} - 1 \right) \text{ cu ft}
\]

All factors of which are available from the combustion tabulation and the Orsat analysis.

The above data, taken together with the flue temperature rise above room temperature permits computation of the flue loss. This is done by multiplying together the volume per cubic foot of fuel gas burned, the specific heat, and the temperature rise of each constituent in the flue products, including XS, and adding these to the latent heat of the water vapor in the products. (The latent heat is taken at room temperature, since the total heating value of the gas is taken on this basis.) When the sum of these heat losses which go up the flue, per cubic foot of the fuel gas burned, is divided by the heating value of a cubic foot of the fuel gas, the quotient is percentage flue loss.

For a typical computation assume the fuel analysis above, an observed CO₂ of 5.0%, room temperature of 80°F, and flue temperature of 380°F.

Compute XS as follows:

\[
X_S = 9.07 \times \left( \frac{12.65}{5.0} - 1 \right) = 12.77 \text{ cu ft}
\]

**Tabulate sensible heat losses:**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Volume</th>
<th>( C_p )</th>
<th>( T_2 - T_1 )</th>
<th>Heat Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>1.09</td>
<td>0.02426</td>
<td>300</td>
<td>7.93</td>
</tr>
<tr>
<td>N₂</td>
<td>7.98</td>
<td>0.01857</td>
<td>300</td>
<td>44.39</td>
</tr>
<tr>
<td>H₂O</td>
<td>2.06</td>
<td>0.02336</td>
<td>300</td>
<td>14.43</td>
</tr>
<tr>
<td>XS</td>
<td>12.77</td>
<td>0.01853</td>
<td>300</td>
<td>70.99</td>
</tr>
</tbody>
</table>

Sensible Heat Loss - - - 137.74 Btu
Latent heat loss equals the volume of water vapor (2.06 cu ft) \times the weight of 1 cu ft at standard conditions (0.4758) \times the latent heat at 80 F (1048) = 102.71.

The total heat loss up the flue is:

137.74 \times 102.71 = 240.45 Btu

and the percentage flue loss is:

109 \times \frac{241}{1069} = 22.6\%

A number of other relationships useful in solving specific problems or in gaining a better understanding of gas combustion processes can be derived from those discussed above. For example, it is convenient to prepare a family of curves in which percent excess air is plotted against observed CO$_2$ for various gases (Fig. 2). The relationship is derived as follows:

$$% XS = 100 \frac{XS}{AR}$$

And since, as we have shown above:

$$XS = VDP x \left( \frac{ULT}{Obs'd CO_2} - 1 \right)$$

$$The \% XS = 100 \times \frac{VDP}{AR} \left( \frac{ULT}{Obs'd CO_2} - 1 \right)$$

Such a chart is convenient in making comparisons of combustion results on the same appliance when changing from one gas to another. Most engineers think in terms of target CO$_2$'s, such as 9.0% on natural gas. The chart gives the equivalent on any other gas for which a curve has been prepared. For example, the percent XS corresponding to 9.0% CO$_2$ on natural gas is 30.0. At this same percent XS the CO$_2$ on propane will be 10.35% and on butane, 10.6% (See Fig. 2).

Another useful stoichiometric relationship which may be derived is that having to do with the combustion "hump", that is, the point at which a lower than normal observed CO$_2$ results from incomplete combustion, with the diversion of part of the fuel carbon into CO. Stoichiometric analysis of combustion reactions will show that this condition is rarely detectable by Osrat CO$_2$ analysis, since the decrease in % CO$_2$ is less than the increase in % CO. That is, with 0.10% CO in the combustion products, the Osrat CO$_2$ will deviate by less than 0.10% from what it would have been with complete combustion. An understanding of this fact will point out that combustion difficulties, where an extreme amount of CO is not present, and where the observed CO$_2$ is not within a fraction of a percent of the ultimate, are much more likely to be due to some such factors as flame impingement or misapplication of combustion air, rather than shortage, per se, of combustion air.
However, by application of stoichiometry and the use of both CO₂ and O₂ Orsat pipettes, it is possible to determine, in the absence of CO analysis equipment, whether combustion is "over the hump". It can be derived from the combustion table that, for a typical natural gas:

\[
\% \text{CO} = \frac{20.9 - \% \text{O}_2 - 1.74 (\% \text{CO}_2)}{0.43 + 0.08 (\% \text{CO}_2)}
\]

Fig 3 was prepared on the basis of the above. As an example of its use, assume a flue gas Orsat analysis of 9.0% CO₂ and 5.6% O₂. This point on the chart indicates 0.20% CO. This represents considerable incomplete combustion; however, if at the same excess air (corresponding to 5.0% O₂) there had been complete combustion, the CO₂ would rise only to 9.1%. This is obviously not an "over the hump" condition in the sense the low CO₂ reading is due to high CO rather than to high excess air. The engineer who realizes this will not waste his time trying to increase excess air, but can look elsewhere for the cause of failure.

Another application of the stoichiometric principles is the evaluation of the effect upon indicated efficiency or flue loss of the introduction of excess air or dilution air. In the flue loss computation above it was shown that the excess air, corresponding to a CO₂ of 5.0% (including draft hood dilution air), carried with it 70.99 Btu per cu ft of gas burned, or approximately 6.6% of the input. Suppose in this example, the CO₂ at the inlet of the draft hood had been 9.0% from which the CS ahead of the draft hood can be computed to be 3.02 cu ft, so that the remaining 12.77 - 3.02 = 9.75 cu ft entered as dilution air. Did this radically affect the flue loss? The answer depends upon the temperature of the dilution air. If it was at room temperature, it carried no heat above room temperature datum with it as it entered the draft hood. It was heated by the flue products with which it mixed, but the heat which it received was given up in exact amount by the products. Consequently, there was no change in Btu per cubic foot of gas burned, above room temperature datum, in the flue products, and the flue loss would be unchanged. On the other hand, if the appliance were a vented recessed heater with the draft hood relief opening in the hot circulating air stream, the condition would be different. Assume dilution air at an average temperature of 200°F, room temperature at 80°F, and the same draft hood dilution (9.75 cu ft air per cu ft gas) as above. In this case, the diluted air would carry into the flue products:

\[
9.75 \times 0.01833 \times 150 = 27.10 \text{ Btu}
\]

per cubic foot of gas burned, increasing the flue loss by

\[
\frac{27.10}{1069} \times 100 = 2.5\%
\]

a not insignificant amount.
As a final example, compute the indicated increase in the loss where the excess air passing through the appliance heat exchanger is increased by the use of the test vent specified for the conduct of the flue loss determinations. (This, in effect, reflects the inefficiency of the draft hood in protecting the appliance against updrafts.) Take an example in which the CO₂ ahead of the draft hood is 9.0% with no vent, but falls to 8.3% when the test vent is added. Assume a flue gas temperature $T_{true}$ at the inlet of the draft hood, of 500°F above room temperature. Compute $X_S$ corresponding to 9.0% and 8.3% CO₂. These volumes for the typical natural gas used, are 3.62 and 4.05 cu ft respectively, or an increase of 1.03 cu ft of XS per cubic foot of gas burned. The increase in flue loss is then:

$$100 \times \frac{1.03 \times 0.01858 \times 500}{1069} = 0.9\%$$

This is not great, but it may be significant on a marginal appliance. Here, the easiest means of improvement might lie in a slight modification of the draft hood.

The above examples show a few of the many ways in which stoichiometry can be put to work in everyday analysis of the problems encountered in laboratory development of a gas burning appliance. As in any field of engineering, a consciousness of underlying principles is the most important tool the engineer can apply to his work. On it depends his analysis of the results obtained and the application of this analysis to development of his product. The point is not that handbook methods, nomographs, and other prepackaged and quick-frozen short cuts are bad; certainly they are extremely valuable timesaving devices. But, unless the engineer understands and is able to apply the principles upon which they are based, he will be at a great disadvantage.
<table>
<thead>
<tr>
<th>Gas</th>
<th>Formula</th>
<th>Specific gravity</th>
<th>Btu per cu ft</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(\text{air} = 1)</td>
<td>Gross</td>
</tr>
<tr>
<td>Acetylene</td>
<td>(\text{C}_2\text{H}_2)</td>
<td>0.921 m</td>
<td>1487.0 c</td>
</tr>
<tr>
<td>Butane</td>
<td>(\text{C}<em>4\text{H}</em>{10})</td>
<td>2.010 m</td>
<td>3271.0 c</td>
</tr>
<tr>
<td>Butylene</td>
<td>(\text{C}_4\text{H}_6)</td>
<td>1.956 m</td>
<td>3679 c</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>(\text{CO}_2)</td>
<td>1.5291 m</td>
<td></td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>(\text{CO})</td>
<td>0.9672 m</td>
<td>323.0 c</td>
</tr>
<tr>
<td>Ethane</td>
<td>(\text{C}_2\text{H}_6)</td>
<td>1.0493 m</td>
<td>1750 s</td>
</tr>
<tr>
<td>Ethylene</td>
<td>(\text{C}_2\text{H}_4)</td>
<td>0.9748 m</td>
<td>1639.0 c</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>(\text{H}_2)</td>
<td>0.0695 m</td>
<td>335.2</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>(\text{H}_2\text{S})</td>
<td>1.1006 m</td>
<td>657.0 m</td>
</tr>
<tr>
<td>Methane</td>
<td>(\text{CH}_4)</td>
<td>0.5545 m</td>
<td>1914.5 a</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>(\text{N}_2)</td>
<td>0.9674 m</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>(\text{O}_2)</td>
<td>1.1054 m</td>
<td></td>
</tr>
<tr>
<td>Pentane</td>
<td>(\text{C}<em>5\text{H}</em>{12})</td>
<td>2.4902 m</td>
<td>4022.0 m</td>
</tr>
<tr>
<td>Pentylene</td>
<td>(\text{C}<em>5\text{H}</em>{10})</td>
<td>2.4208 m</td>
<td>3835.0 m</td>
</tr>
<tr>
<td>Propane</td>
<td>(\text{C}_3\text{H}_8)</td>
<td>1.5625 m</td>
<td>2586.0 c</td>
</tr>
<tr>
<td>Propylene</td>
<td>(\text{C}_3\text{H}_6)</td>
<td>1.4528 m</td>
<td>2345.0 c</td>
</tr>
<tr>
<td>Water vapor</td>
<td>(\text{H}_2\text{O})</td>
<td>0.6214 m</td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td></td>
<td>1.00</td>
<td></td>
</tr>
</tbody>
</table>

m - Bureau of Mines value

** - Combustion by A.G.A.

s - Calculated values

a - Laboratory value figured from Bull. 139 U. of Ill.

s - Smithsonian Inst. tables.

Values from combustion, Bureau of Mines Bulletin 197, Gas Chemists Handbook, Smithsonian Tables, Van Nostrand's Chemical Rubber Handbook, Bull. 139 U. of Ill. Where these authorities did not agree, the values were recalculated from the original data.