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ERRATA

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This errata is issued to correct a typographical error.

page 5:  The value of $a_2$ should read  -2.9745, instead of 2.9745.

# New Method for Determining Heats of Combustion of Gaseous Hydrocarbons

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## Summary

As a spin-off of a system developed for monitoring and controlling the oxygen concentration in the Langley 8-Foot High-Temperature Tunnel, a highly accurate on-line technique has been developed for determining heats of combustion of natural gas samples. It is based on measuring the ratio $m/n$, where $m$ is the (volumetric) flowrate of oxygen required to enrich the carrier air in which the test gas flowing at the rate $n$ is burned, such that the mole fraction of oxygen in the combustion product gases equals that in the carrier air. The $m/n$ ratio is directly related to the heats of combustion of the saturated hydrocarbons present in the natural gas.

A measurement of the $m/n$ ratio for the test gas can provide a direct means of determination of its heat of combustion by using the calibration graph relating the $m/n$ values for pure saturated hydrocarbons with their heats of combustion. The accuracy of the technique is determined solely by the accuracy with which the flowrates $m$ and $n$ can be measured and is of the order of 2 percent in the present study. The theoretical principles and experimental results are discussed.

## Introduction

We recently developed a system for monitoring and controlling the oxygen concentration in the Langley 8-Foot High-Temperature Tunnel (ref. 1). It is based on a $Y_2O_3$-stabilized $ZrO_2$ electrochemical sensor. The system is capable of maintaining oxygen concentration at $20.9 \pm 1.0$ percent in the methane-oxygen-air combustion product gases. During the development of the system, it was noted that the degree of the required oxygen enrichment of the air was very strongly dependent on the purity of the combustible gas ($CH_4$). For example, it was noted that the presence of traces of noncombustible components—such as $N_2$, $CO_2$, or $H_2O$— noticeably affected the amount of oxygen that needed to be added to the air to make the mole fraction of oxygen, $X(O_2)$, in the combustion product gases equal to that in the standard air. It was quickly realized that the reverse was also true, that is, the purity of the combustible test gas could be inferred by measuring the amount of oxygen needed for $X(O_2)$ equalization (ref. 2). It is now demonstrated that the technique can be further extended to infer the presence of heavier saturated hydrocarbons in the combustible test gas (natural gas) as well. It is assumed that saturated varieties are the only types of hydrocarbons found in the natural gas samples. According to reference 3, saturated hydrocarbons are the predominant varieties present in U.S. natural gas samples. Since the heat of combustion of natural gas

depends on its effective hydrocarbon content, measurement of the amount of oxygen needed for $X(O_2)$ equalization can be used for direct determination of the thermal content of the test gas (natural gas). Details of the theory of operation of the new system and the experiments conducted to verify its accuracy are discussed in the following sections.

The heats of combustion of gaseous hydrocarbons are presently determined by using a constant pressure flame calorimeter (ref. 4). However, calorimetric measurements cannot be made on-line and require information about the thermal properties of the combustion products of the test sample. The technique reported here, on the other hand, is direct, can be performed on-line, and requires no prior knowledge about the composition of the test sample.

## Symbols

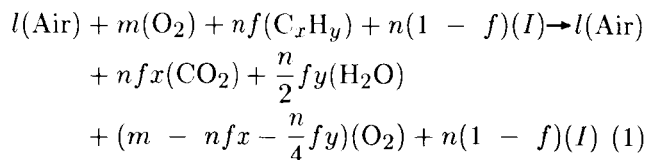| | |
|---|---|
| $A$ | $= 4\,X(O_2)(1-f) + f\{4x + [1 + X(O_2)]y\}$ |
| | $= 4x + [1 + X(O_2)]y \quad$ for $f = 1$ |
| | $= 4\,X(O_2) \quad$ for $f = 0$ |
| | $A$ depends only on the composition of the test gas and the mole fraction of oxygen in the air used for combustion |
| $C_xH_y$ | hydrocarbon (for saturated hydrocarbons, $y = 2x + 2$) |
| $f$ | combustible fraction of test gas |
| $I$ | noncombustible impurities (such as $N_2$, $CO_2$, and $H_2O$) in test gas |
| $l$ | volumetric flowrate of carrier air stream |
| $m$ | volumetric flowrate of oxygen |
| $n$ | volumetric flowrate of test gas (mixture of saturated hydrocarbons and noncombustible impurities) |
| sccm | standard cubic centimeters per minute; values listed are for $20°C$ and 101.3 kPa |
| $X(O_2)$ | mole fraction of oxygen |
| $\alpha$ | $m/n$ for $X(O_2) = 0.2095$ (standard air) |
| $\Delta H$ | heat of combustion |

## Theoretical Principles

A general expression for the combustion of a natural gas sample in oxygen-enriched air can be

written as follows:

$$l(\text{Air}) + m(O_2) + nf(C_xH_y) + n(1 - f)(I) \rightarrow l(\text{Air})$$
$$+ nfx(CO_2) + \frac{n}{2}fy(H_2O)$$
$$+ (m - nfx - \frac{n}{4}fy)(O_2) + n(1 - f)(I) \quad (1)$$

where

$C_xH_y + I$     test gas

$C_xH_y$     effective hydrocarbon in test gas

$I$     noncombustible impurities in test gas

$f$     combustible fraction of test gas

The mole fraction of oxygen in the products of equation (1) is given by

$$X(O_2) = \frac{0.2095l + \left[m - \frac{nf}{4}(4x + y)\right]}{l + nfx + \frac{n}{2}fy + \left[m - \frac{nf}{4}(4x + y)\right] + n(1 - f)}$$
$$= \frac{0.2095l + \left[m - \frac{nf}{4}(4x + y)\right]}{l + m + n + nf\left(\frac{y - 4}{4}\right)} \quad (2)$$

If $X(O_2) = 0.2095$, we obtain

$$\frac{0.838(1 - f) + f(4x + 1.2095y)}{3.162} = \frac{m}{n} \quad (3)$$

If $f = 1$ (i.e., the test gas has *no* noncombustible impurities), equation (3) reduces to

$$\frac{4x + 1.2095y}{3.162} = \frac{m}{n} = \alpha \quad (4)$$

This equation is identical to equation (6) in reference 2. If, on the other hand, $f = 0$ (i.e., no combustible fraction is present in the test gas), equation (3) reduces to

$$0.2650 = \frac{m}{n} \quad (5)$$

Generalizing equation (3) for nonstandard air, we obtain

$$\frac{4X(O_2)(1 - f) + f\{4x + [1 + X(O_2)]y\}}{4[1 - X(O_2)]}$$
$$= \frac{A}{4[1 - X(O_2)]} = \frac{m}{n} \quad (6)$$

TABLE I. SUMMARY OF m/n VALUES FOR SELECTED SATURATED HYDROCARBONS

$[X(O_2) = 0.2042 \text{ and } 0.2095]$

| Hydrocarbon | Chemical formula | $m/n$ for | |
|---|---|---|---|
| | | $X(O_2) =$ 0.2042 | $X(O_2) =$ 0.2095 |
| Methane | $CH_4$ | 2.770 | 2.795 |
| Ethane | $C_2H_6$ | 4.783 | 4.825 |
| Propane | $C_3H_8$ | 6.796 | 6.855 |
| Butane | $C_4H_{10}$ | 8.809 | 8.885 |
| Pentane | $C_5H_{12}$ | 10.823 | 10.915 |
| Hexane | $C_6H_{14}$ | 12.836 | 12.945 |
| Heptane | $C_7H_{16}$ | 14.849 | 14.975 |
| Octane | $C_8H_{18}$ | 16.862 | 17.005 |
| Nonane | $C_9H_{20}$ | 18.875 | 19.035 |
| Decane | $C_{10}H_{22}$ | 20.888 | 21.065 |

The values of $m/n$ for some of the pure saturated hydrocarbons in standard and nonstandard air are summarized in table I.

Figure 1 shows the correlation between $A$ and $m/n$ for selected saturated hydrocarbons. It is apparent that $A$ and $m/n$ are linearly related. If $f \neq 1$, $m/n$ values for various impurity-containing hydrocarbon gases will be different from those for pure hydrocarbons. An experimental measurement of $m/n$ will then give $f$, the combustible fraction in the test gas. The correlation between $A$ and $m/n$ for binary gas mixtures is shown in figure 2. Figures 1 and 2 clearly demonstrate that the $m/n$ values for gases containing saturated hydrocarbons are uniquely related to their hydrogen and carbon contents.
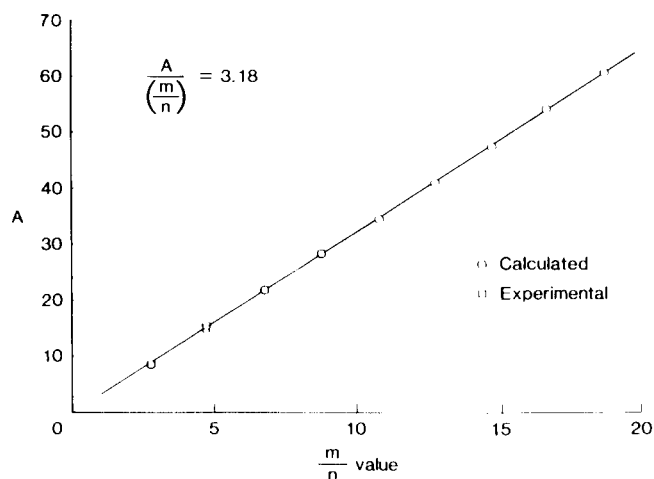


Figure 1. $A$ as a function of $m/n$ for pure unbranched acyclic hydrocarbons. $X(O_2) = 0.2042$; $A = 4 X(O_2) (1 - f) + f\{4x + [1 + X(O_2)]y\}$.
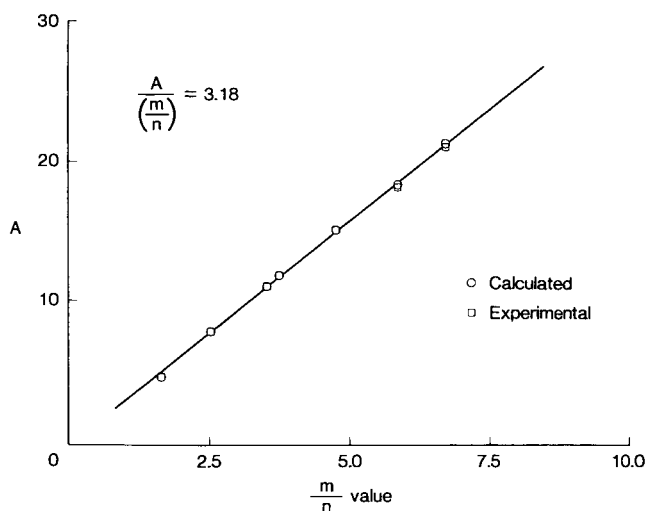
Figure 2. $A$ as a function of $m/n$ for binary mixtures of saturated hydrocarbons and noncombustible gases. $X(O_2) = 0.2042; A = 4\ X(O_2)(1 - f) + f\{4x + [1 + X(O_2)]y\}$.

If the test gas is not a pure single hydrocarbon but is a mixture of two or more hydrocarbons, equation (6) can be used to readily calculate the $m/n$ value for the "effective" test hydrocarbon. For example, for a test gas containing equal mole fractions of $CH_4$ and $C_2H_6$, the effective equivalent hydrocarbon would be $C_{1.5}H_{5.0}$, giving $m/n = 3.81$ for $X(O_2) = 0.2095$. If this mixture also contained an incombustible impurity, the corresponding $m/n$ value would be lower, as indicated by equation (6). Figure 3 shows $A$ as a function of $m/n$ for $f \neq 1$ for test gases containing several saturated hydrocarbons as well as noncombustible gases. Again the uniqueness of the correlation between $A$ and $m/n$ is evident.

Because $m/n$ values for various test gases containing saturated hydrocarbons are related to their chemical composition, they can serve as the basis for direct determination of heats of combustion. Table II lists the gross heats of combustion of several pure saturated hydrocarbons (refs. 5–8).

Figure 4 shows heat of combustion (in kilocalories per mole) versus $m/n$ value for several selected saturated hydrocarbons. Similar results for mixtures containing selected saturated hydrocarbons and noncombustible gases are illustrated in figure 5. It is apparent that the heats of combustion of various gases are directly related to their corresponding $m/n$ values. An experimental determination of $m/n$ for the test gas is, therefore, expected to provide an on-line determination of its heat of combustion.
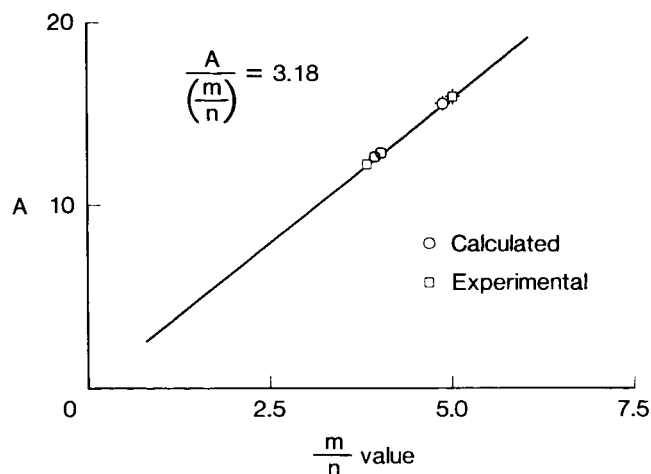


Figure 3. $A$ as a function of $m/n$ for complex mixtures of saturated hydrocarbons and noncombustible gases. $X(O_2) = 0.2042; A = 4\ X(O_2)(1 - f) + f\{4x + [1 + X(O_2)]y\}$.

TABLE II. GROSS HEATS OF COMBUSTION $\Delta H$ OF SELECTED SATURATED HYDROCARBONS

| Hydrocarbon | $m/n$ [$X(O_2) = 0.2095$] | $\Delta H$, kcal/mol | $\frac{\Delta H}{m/n}$, kcal/mol |
|---|---|---|---|
| $CH_4$ | 2.795 | 212.80 | 76.14 |
| $C_2H_6$ | 4.825 | 372.82 | 77.27 |
| $C_3H_8$ | 6.855 | 530.61 | 77.40 |
| $C_4H_{10}$ | 8.885 | 687.65 | 77.39 |
| $C_5H_{12}$ | 10.915 | 845.10 | 77.43 |
| $C_6H_{14}$ | 12.945 | 1002.55 | 77.45 |
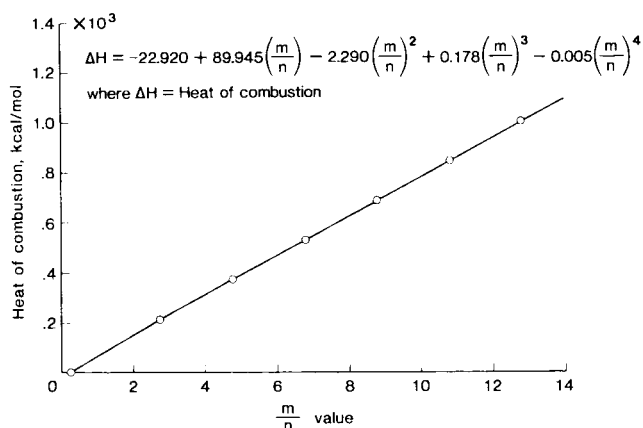


Figure 4. Heats of combustion versus $m/n$ values for saturated hydrocarbons. $X(O_2) = 0.2042$.

3

$$\Delta H = -22.690 + 90.268\left(\frac{m}{n}\right) - 2.450\left(\frac{m}{n}\right)^2 + 0.210\left(\frac{m}{n}\right)^3 - 0.006\left(\frac{m}{n}\right)^4$$

where $\Delta H$ = Heat of combustion
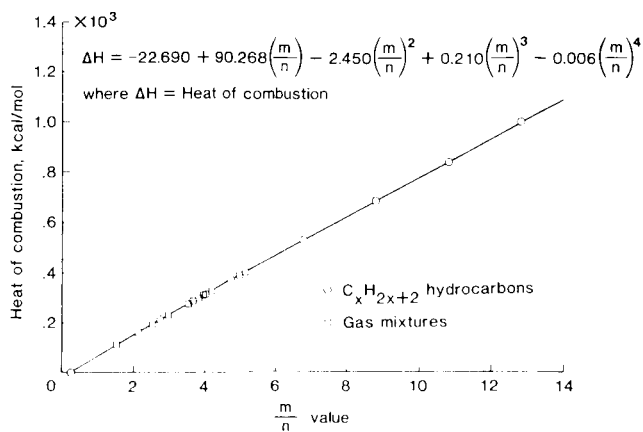
• $C_xH_{2x+2}$ hydrocarbons

□ Gas mixtures

Figure 5. Heats of combustion versus $m/n$ values for gas mixtures containing saturated hydrocarbons and noncombustible impurities. $X(O_2) = 0.2042$.

## Experimental Procedures and Results

The experimental plan involved measuring $m/n$ values for the following kinds of test gas samples:

1. Pure saturated gaseous hydrocarbons (methane, ethane, propane, butane, etc.)

2. Binary mixtures of selected saturated hydrocarbons (i.e., no noncombustible components)

3. Binary mixtures containing a saturated hydrocarbon and an inert gas

4. Gaseous mixtures containing several saturated hydrocarbons and selected noncombustible impurities.

Figure 6 shows a schematic diagram of the experimental system used for measuring $m/n$ values for the test gas samples (refs. 1 and 2).
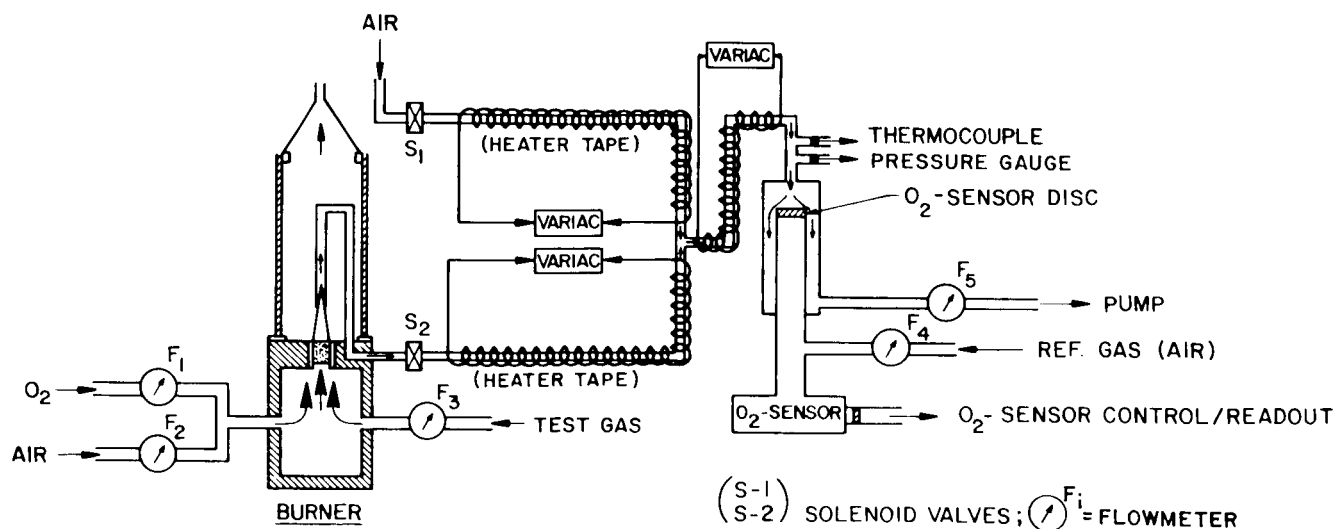
## Determination of $m/n$ Values for Pure Hydrocarbon Gases

Since $m/n$ values are strongly dependent on the mole fraction of oxygen, $X(O_2)$, pure bottled dry air was used to supply the carrier air stream. A gas chromatographic analysis of this air gave an $X(O_2)$ value of $0.2042 \pm 0.0050$. The $ZrO_2$ sensor output was first recorded for the carrier air stream. Next, the products of combustion of selected hydrocarbons in oxygen-enriched air were directed through the $O_2$-sensing system. The oxygen flowrate $(m)$ was adjusted until the $ZrO_2$ sensor output matched that for air. These measurements were repeated for a number of hydrocarbon flowrates $(n)$ while the air flowrate $(l)$ was held constant. It should perhaps be emphasized that $n$ in the parameter $m/n$ represents the volume flowrate for the test gas rather than the conventional mass flowrate. It will therefore be necessary to use a volume flowmeter for metering the test gas flowrate. We used a positive displacement dry test meter for measuring the true volume flowrate $(n)$ of the test gases. A dry test meter was preferred over the wet test meter, since the latter would allow the test gases to come in contact with water (or some other selected fluid) during passage through the meter and thereby affect the combustible fraction in the test sample. Three gases with widely different thermal characteristics were used to measure the accuracy with which the dry test meter measured their flowrates. The data summarized in table III demonstrate that the dry test meter gives as accurate a volume flowrate value as the widely used thermal mass flowmeters. A comparison of the experimental and the calculated values for various saturated hydrocarbons is given in table IV.



AIR

VARIAC

THERMOCOUPLE
PRESSURE GAUGE
$O_2$-SENSOR DISC

(HEATER TAPE)

VARIAC

VARIAC

$S_1$

$S_2$

(HEATER TAPE)

$F_5$ → PUMP

$F_4$ → REF. GAS (AIR)

$F_1$

$F_2$

$F_3$

$O_2$ →

AIR →

TEST GAS

$O_2$-SENSOR → $O_2$- SENSOR CONTROL/READOUT

BURNER

$\begin{pmatrix} S-1 \\ S-2 \end{pmatrix}$ SOLENOID VALVES; $\left(\!/\right)^{F_i}$ = FLOWMETER

Figure 6. Experimental system for determining heats of combustion of hydrocarbon gases.

## TABLE III. COMPARISON OF DRY TEST METER AND THERMAL MASS FLOWMETER FLOWRATES IN THE RANGE OF 500–1500 sccm

| Test gas | Flowrates, sccm, measured by – | |
| --- | --- | --- |
| | Dry test meter[a] | Thermal mass flowmeter[b] |
| Air | 999.3 ± 10.0 | 994.6 ± 10.0 |
| | 792.3 ± 10.0 | 794.7 ± 10.0 |
| | 651.8 ± 10.0 | 646.0 ± 10.0 |
| | 502.7 ± 10.0 | 499.9 ± 10.0 |
| Helium | 1400.0 ± 10.0 | 1413.3 ± 14.3 |
| | 1118.7 ± 10.0 | 1119.3 ± 14.3 |
| | 840.7 ± 10.0 | 842.1 ± 14.3 |
| | 557.6 ± 10.0 | 558.1 ± 14.3 |
| Carbon dioxide | 729.0 ± 10.0 | 731.9 ± 7.4 |
| | 636.4 ± 10.0 | 629.3 ± 7.4 |
| | 518.5 ± 10.0 | 512.8 ± 7.4 |

[a]Errors in the dry test meter flowrates are based on uncertainties in the time required for the flow of preset volumes.

[b]Errors in the mass flowmeter flowrates represent 1 percent of the full scale of the meter (Full scale = 1000 sccm).

### Determination of $m/n$ Values for Test Gas Mixtures

Values of $m/n$ for various test gas mixtures were determined in exactly the same way as for pure hydrocarbons. The test gas flowrates were calculated by using a flowrate conversion factor computed on the basis of known test gas composition (ref. 9). These computed flowrates were in agreement with the values obtained by direct measurements with a positive displacement dry test meter. The results for the various test gas mixtures are summarized in table V.

From the data summarized in tables IV and V, it is apparent that the calculated and experimental values of $m/n$ for various types of mixtures are in excellent agreement. As indicated earlier, the $m/n$ values for the mixtures can be used to infer their heats of combustion. The reported (refs. 5–8) gross heat of combustion values for saturated hydrocarbons listed in table II were used to derive the following relationship between $m/n$ values and heat of combustion expressed in kilocalories per mole:

$$\text{Heat of combustion} = a_0 + a_1\frac{m}{n} + a_2\left(\frac{m}{n}\right)^2 + a_3\left(\frac{m}{n}\right)^3 + a_4\left(\frac{m}{n}\right)^4$$

where

$a_0 = -23.2134$
$a_1 = 91.2088$
$a_2 = 2.9745$
$a_3 = 0.3032$
$a_4 = -0.0117$

In developing this equation, a statistical weight of 5 was assigned to $m/n = 0.2566 \approx 0.26$ ($f = 0$; $X(O_2) = 0.2042$) to reflect the fact that the heat of combustion of a noncombustible mixture is definitely zero, whereas the heats of combustion of other mixtures are not known as accurately. A comparison between the heat of combustion values determined from experimentally observed $m/n$ values and those calculated from known chemical compositions is given in table VI. It is apparent from the results summarized in table VI that the agreement between the experimental and the calculated values of heat of combustion for the various gas mixtures is excellent.

## TABLE IV. SUMMARY OF EXPERIMENTAL AND CALCULATED $m/n$ VALUES FOR SELECTED HYDROCARBONS IN AIR

$[X(O_2) = 0.2042]$

| Test hydrocarbon | Hydrocarbon flowrate,[a] $n$, sccm | Equalizing oxygen flowrate,[a] $m$, sccm | Carrier air flowrate,[a] $l$, sccm | $m/n$ value | |
| --- | --- | --- | --- | --- | --- |
| | | | | Experimental | Calculated (from eq. (6)) |
| $CH_4$ | 71.80 ± 0.72 | 200.80 ± 1.00 | 500.0 | 2.797 ± 0.042 | 2.770 |
| $C_2H_6$ | 45.85 ± 0.46 | 214.67 ± 1.00 | 500.0 | 4.682 ± 0.070 | 4.783 |
| $C_3H_8$ | 29.18 ± 0.30 | 199.71 ± 1.00 | 500.0 | 6.843 ± 0.103 | 6.796 |
| $C_4H_{10}$ | 24.20 ± 0.24 | 213.00 ± 1.00 | 500.0 | 8.801 ± 0.132 | 8.809 |

[a] The sccm values are for 20°C and 101.3 kPa. The accuracies of the flowrates reflect ±1 percent of the full scale of the flowmeters.

## TABLE V. SUMMARY OF EXPERIMENTAL AND CALCULATED $m/n$ VALUES FOR VARIOUS TEST GAS MIXTURES

$$[X(O_2) = 0.2042]$$

| Test gas mixture, percent volume | Mixture flowrate,[a] $n$, sccm | Equalizing oxygen flowrate,[a] $m$, sccm | Carrier air flowrate,[a] $l$, sccm | $m/n$ value Experimental | $m/n$ value Calculated[b] |
|---|---|---|---|---|---|
| Binary mixtures | | | | | |
| 50.10% $CH_4$ + 49.90% $C_2H_6$ | 96.00 ± 0.83 | 362.3 ± 1.0 | 500.0 | 3.774 ± 0.043 | 3.770 ± 0.044 |
| 50.19% $CH_4$ + 49.81% $C_3H_8$ | 68.70 ± 0.75 | 326.4 ± 1.0 | 500.0 | 4.751 ± 0.066 | 4.783 ± 0.065 |
| 50.40% $CH_4$ + 49.60% $C_4H_{10}$ | 56.18 ± 0.75 | 322.0 ± 1.0 | 500.0 | 5.732 ± 0.092 | 5.789 ± 0.094 |
| 51.39% $C_2H_6$ + 48.61% $C_4H_{10}$ | 52.58 ± 0.53 | 353.0 ± 1.0 | 500.0 | 6.713 ± 0.087 | 6.740 ± 0.030 |
| 50.13% $CH_4$ + 49.87% $N_2$ | 100.30 ± 1.23 | 153.5 ± 1.0 | 500.0 | 1.530 ± 0.028 | 1.517 ± 0.034 |
| 50.08% $CH_4$ + 49.92% $CO_2$ | 100.40 ± 1.01 | 153.3 ± 1.0 | 500.0 | 1.527 ± 0.025 | 1.515 ± 0.031 |
| 49.92% $C_2H_6$ + 50.08% $N_2$ | 99.80 ± 1.10 | 252.2 ± 1.0 | 500.0 | 2.526 ± 0.038 | 2.516 ± 0.026 |
| 49.87% $C_2H_6$ + 50.13% $CO_2$ | 99.90 ± 0.84 | 253.0 ± 1.0 | 500.0 | 2.531 ± 0.031 | 2.514 ± 0.023 |
| 49.96% $C_3H_8$ + 50.04% $N_2$ | 99.90 ± 1.05 | 353.3 ± 1.0 | 500.0 | 3.536 ± 0.040 | 3.524 ± 0.021 |
| 49.91% $C_3H_8$ + 50.09% $CO_2$ | 100.00 ± 0.78 | 354.3 ± 1.0 | 500.0 | 3.542 ± 0.037 | 3.521 ± 0.018 |
| Complex mixtures[c] | | | | | |
| 44.63% $C_2H_6$ + 25.88% $C_3H_8$ + 10.81% $C_4H_{10}$ + 5.09% $CO_2$ + 13.59% $N_2$ | 39.7 ± 0.4 | 199.0 ± 1.0 | 500.0 | 5.014 ± 0.075 | 4.894 ± 0.083 |
| 53.04% $CH_4$ + 26.09% $C_2H_6$ + 18.42% $C_3H_8$ + 1.43% $CO_2$ + 1.01% $N_2$ | 49.9 ± 0.5 | 198.0 ± 1.0 | 500.0 | 3.968 ± 0.060 | 3.975 ± 0.034 |
| 50.84% $CH_4$ + 17.12% $C_2H_6$ + 24.87% $C_3H_8$ + 3.34% $CO_2$ + 3.83% $N_2$ | 50.3 ± 0.5 | 193.0 ± 1.0 | 500.0 | 3.837 ± 0.057 | 3.936 ± 0.046 |
| 51.51% $CH_4$ + 21.24% $C_2H_6$ + 23.82% $C_3H_8$ + 1.74% $CO_2$ + 1.69% $N_2$ | 49.2 ± 0.5 | 199.5 ± 1.0 | 500.0 | 4.055 ± 0.061 | 4.070 ± 0.036 |

[a] The sccm values are for 20°C and 101.3 kPa. The accuracies of the flowrates reflect ±1 percent of the full scale of the flowmeter.

[b] The errors in the calculated values results from errors in the mixture composition.

[c] The accuracies of the concentrations are of the order of ±1 percent of the values listed.

TABLE VI. COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES OF
GROSS HEAT OF COMBUSTION $\Delta H$ FOR VARIOUS GAS MIXTURES

| Mixture composition, volume percent | $\Delta H$, kcal/mol | |
| --- | --- | --- |
| | Experimental[a] | Calculated[b] |
| Binary mixtures | | |
| 50.10% $CH_4$ + 49.90% $C_2H_6$ | 292.6 ± 3.4 | 292.2 ± 3.9 |
| 50.19% $CH_4$ + 49.81% $C_3H_8$ | 369.5 ± 5.2 | 371.1 ± 5.2 |
| 50.40% $CH_4$ + 49.60% $C_4H_{10}$ | 446.3 ± 7.4 | 449.2 ± 2.2 |
| 50.13% $CH_4$ + 49.87% $N_2$ | 110.6 ± 2.2 | 109.0 ± 2.8 |
| 50.08% $CH_4$ + 49.92% $CO_2$ | 110.4 ± 2.2 | 109.4 ± 2.6 |
| 49.92% $C_2H_6$ + 50.08% $N_2$ | 193.0 ± 3.1 | 192.2 ± 2.2 |
| 49.87% $C_2H_6$ + 50.13% $CO_2$ | 193.4 ± 2.6 | 192.0 ± 1.8 |
| 49.96% $C_3H_8$ + 50.04% $N_2$ | 274.3 ± 3.8 | 273.3 ± 1.6 |
| 49.91% $C_3H_8$ + 50.09% $CO_2$ | 274.7 ± 3.0 | 273.0 ± 1.4 |
| Complex mixtures | | |
| 44.63% $C_2H_6$ + 25.88% $C_3H_8$ + 10.81% $C_4H_{10}$ + 5.09% $CO_2$ + 13.59% $N_2$ | 390.1 ± 11.7 | 380.6 ± 9.9 |
| 53.04% $CH_4$ + 26.09% $C_2H_6$ + 18.42% $C_3H_8$ + 1.43% $CO_2$ + 1.01% $N_2$ | 307.7 ± 7.8 | 308.3 ± 8.0 |
| 50.84% $CH_4$ + 17.12% $C_2H_6$ + 24.87% $C_3H_8$ + 3.34% $CO_2$ + 3.83% $N_2$ | 297.4 ± 5.6 | 305.4 ± 8.0 |
| 51.51% $CH_4$ + 21.24% $C_2H_6$ + 23.82% $C_3H_8$ + 1.74% $CO_2$ + 1.69% $N_2$ | 311.5 ± 8.0 | 315.9 ± 8.3 |

[a] The experimental values of heat of combustion were obtained by using the experimentally measured $m/n$ values. The errors in these heat of combustion values result from errors in the $m/n$ values.

[b] The calculated values of heat of combustion were obtained from the known mixture compositions. The errors in these values result from the errors in the mixture composition.

TABLE VII. COMPOSITION OF NATURAL GAS SAMPLE

| Component[a] | Volume percent[b] | Component[a] | Volume percent[b] |
|---|---|---|---|
| $CH_4$ | 95.91 | $C_5H_{12}$ | 0.10 |
| $C_2H_6$ | 2.14 | $C_6H_{14}$ | 0.01 |
| $C_3H_8$ | 0.37 | $CO_2$ | 0.84 |
| $C_4H_{10}$ | 0.20 | $N_2$ | 0.43 |

[a] No measurable concentrations of $O_2$ or $C_5H_{10}$ were found in the natural gas sample tested in this study, though traces of these gases have been reported in natural gas samples from other sources (ref. 3).

[b] The accuracies of the concentrations are of the order of ±2 percent of the values listed.

## Verification of Computational Procedure

The gas selected for the verification test was a sample of natural gas supplied to Langley Research Center by the Virginia Natural Gas Company (VNG). Its flowrate ($n$) was measured with the dry test flowmeter, and the corresponding $m/n$ value was determined in the manner explained earlier. The test gas was later analyzed by gas chromatography (ref. 2), and its $m/n$ value was computed on the basis of its measured chemical composition, which is given in table VII. It should be noted that the only combustibles present in the VNG sample were saturated hydrocarbons. There were no measurable concentrations of $H_2$, $O_2$, and $C_5H_{10}$. This is consistent with a recent Bureau of Mines study (ref. 3), in which it was found that the concentrations of $H_2$, $O_2$, and $C_5H_{10}$ in almost all the natural gas samples analyzed in 1982 were ≤ 0.1 mole percent. A comparison between the experimental and computed tables of $m/n$ is summarized in table VIII. Also included in this table are the computed and experimentally determined values of the gross heat of combustion. The agreement between corresponding values is excellent.

TABLE VIII. COMPARISON OF COMPUTED AND EXPERIMENTALLY DETERMINED VALUES OF $m/n$ AND HEAT OF COMBUSTION FOR THE NATURAL GAS SAMPLE

| Parameter | Computed | Experimental |
|---|---|---|
| $m/n$ . . . . . . . . . | 2.84 ± 0.03 | 2.85 ± 0.01 |
| $\Delta H$, kcal/mol . . . | 218.8 ± 2.2 | 218.5 ± 1.1 |

## Concluding Remarks

A new technique has been developed for determining heats of combustion of test gases containing saturated hydrocarbons. It is based on the measurement of the $m/n$ ratio, where $m$ is the volumetric flowrate of oxygen needed to enrich the carrier air in which the test gas flowing at the rate $n$ is burned, so that the mole fraction of oxygen in the combustion product gases equals that in the carrier air. The $m/n$ values are directly related to the heats of combustion of the test gases. The accuracy of the derived values of heat of combustion is determined solely by the accuracies with which the flowrates $m$ and $n$ can be measured. At the flowrates used in the present study, the respective accuracies are of the order of 1 percent. This leads to an error in the heats of combustion of the order of 2 percent.

The heats of combustion of hydrocarbons are presently determined by using a constant volume bomb calorimeter for liquids and solids and a constant pressure flame calorimeter for gases. These measurements can be very accurate (<1 percent), since they depend mainly on the bath temperature measurement. However, calorimetric measurements cannot be made on-line and require information about the thermal properties of the combustion products of the test sample. The technique reported here, on the other hand, is direct, can be performed on-line, and requires no prior knowledge about the exact composition of the test sample. (The only assumption made regarding the composition is that saturated hydrocarbons are the only combustibles present in the test samples.) It thus appears that this new technique may be more useful for field operations where on-line measurements of the heats of combustion of the test gases are often needed.

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15. Supplementary Notes

16. Abstract

As a spin-off of a system developed for monitoring and controlling the oxygen concentration in the Langley 8-Foot High-Temperature Tunnel, a highly accurate on-line technique has been developed for determining heats of combustion of natural gas samples. It is based on measuring the ratio $m/n$, where $m$ is the (volumetric) flowrate of oxygen required to enrich the carrier air in which the test gas flowing at the rate $n$ is burned, such that the mole fraction of oxygen in the combustion product gases equals that in the carrier air. The $m/n$ ratio is directly related to the heats of combustion of the saturated hydrocarbons present in the natural gas. A measurement of the $m/n$ ratio for the test gas can provide a direct means of determination of its heat of combustion by using the calibration graph relating the $m/n$ values for pure saturated hydrocarbons with their heats of combustion. The accuracy of the technique is determined solely by the accuracy with which the flowrates $m$ and $n$ can be measured and is of the order of 2 percent in the present study. The theoretical principles and experimental results are discussed.

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