USE OF AN EMISSION ANALYZER TO DEMONSTRATE BASIC PRINCIPLES

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In choosing and developing experiments for undergraduate laboratories, instructors often try to avoid those experiments that require lengthy or sophisticated chemical analysis, such as experiments related to environmental engineering. But the development of electrochemical and infrared sensors has made gas analysis much easier to accomplish.

This paper describes experiments based on the use of a portable stack gas analyzer, or emission analyzer. In a sense, the analyzer is modern technology's replacement for the classical Orsat analysis of flue gases;[1] but the analyzer does not measure carbon dioxide levels directly, calculating them instead from the knowledge of fuel type using basic stoichiometry. The modern analyzer provides a relatively quick and painless way of doing chemical analysis for a gaseous system.

The analyzer used here costs $6,350 and was purchased under an NSF-ILI grant.[2] With the additional purchase of other more modest components for about $250, simple combustion experiments with a laboratory burner and a makeshift flue were run. The results were used to demonstrate: 1) the principles of a rotameter, 2) material balances based on the measured molar flow of the fuel gas and the measured volume fraction of oxygen in the exiting flue gases, 3) energy balances based on the temperature of the exiting flue gases, and 4) how the kinetics of nitric oxide formation can be used to estimate temperatures in the hottest part of the flame.

The chemical engineering program at the University of Minnesota, Duluth, is relatively small, with five full-time faculty, three temporary instructors, and a graduating class in the range of 20-30 students. Without the amenities of larger departments (*e.g.*, shop facilities), it is difficult to develop experiments requiring considerable construction of apparatus or faculty time. The experiment described here is relatively straightforward to do—the analyzer does the hard work. It is intended as an undergraduate experiment, however, and should not be construed as a research-level experiment or an experiment with which to do thorough studies of combustion.

The analyzer is self-contained in a carrying case the size of a large brief case, so storage of the experiment's components is not a problem. The department also offers a minor in environmental engineering, and the intention is to use this analyzer in a new environmental-engineering laboratory course; other experiments for this course have been described elsewhere.[3] A group of our students used the analyzer as part of their project in our capstone design course and the project was successfully entered in a national competition.[4]

EXPERIMENTAL

The apparatus comprises a section of double-walled galvanized flue pipe (18 in long and 3 in wide) mounted vertically with a flue cap positioned on top; these items were purchased from a hardware store. A Veriflow burner, fitted with an N-2 nozzle (Fisher Scientific) was positioned at the center of the bottom opening of the flue; it was connected via a rotameter (Cole Parmer E-32461-58), calibrated in liters of air per minute (L air/min), to the laboratory supply of natural gas. To obtain temperatures in the exiting flue gas that vary with the flow of natural gas, controlled by the rotameter, it was essential to restrict the flow of air into the bottom of the flue. A can of suitable dimensions was cut in

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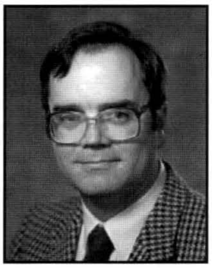

half, and a 1-in square hole was punched in the bottom of one half. This half was fitted into the bottom of the flue and the burner was positioned at the center of the hole. The rotameter was calibrated with a household gas meter (Equipmeter S-275). For the experiments described here, air was not premixed with natural gas before entering the burner, so the combustion was controlled by diffusion of air.[5]

The emission analyzer is a COSA 6000 portable stack gas analyzer. This measures the volume fractions of O_2, CO, NO_x, and SO_x using electrochemical cells. (The lifetime of the O_2 cell is the most limited, being in the range of 1-2 years; the other cells will last between 2 and 3 years.) The analyzer pumps the gas to be sampled through the end of a hollow metal probe (12 in long) at the tip of which is a thermocouple (type K) for measuring the gas temperature. The gas passes from the metal probe via flexible tubing (10 ft long) to a condensate trap clamped to the outside of the main case containing the analytical components of the analyzer. This passage of the gas to the analyzer results in the gas entering the train of electrochemical cells at essentially ambient temperature.

From the measurements of gas levels and temperature, the instrument's firmware calculates various quantities. The volume fraction of CO_2 and the excess air are of most concern here. This requires the user to select the fuel type; the selection includes natural gas, propane, butane, coal, oils light no. 2 and no. 6, as well as a programmable option. Other calculated quantities include efficiency and effectiveness; these are not considered here.

For the experiments described here, the tip of the probe was positioned just below the center of the flue cap. Two to four sets of data for each of six different flows of natural gas were collected. It was important to let the rotameter setting stabilize after changing it. The data presented here were comfortably obtained within 3 to 4 hours; the treatment of the data may take most students a lot longer!

RESULTS AND INTERPRETATION

Calibration of the Rotameter • Volumetric flows were measured under ambient conditions (25°C and 1 atm) throughout. The volumetric flow rate of natural gas, V_{ng}, read directly from the household gas meter in units of ft^3/min, regressed against the reading of the rotameter, V_{air}, in units of L/min leads to

$$V_{ng}\left(ft^3/\min\right)=(0.0504\pm0.0005)V_{air}(L/\min)\quad r^2=0.987 \tag{1}$$

This is transformed to

$$V_{ng}(L/\min)=(1.43\pm0.01)V_{air}(L/\min) \tag{2}$$

What useful information can we obtain from the value of the slope? The theory of the rotameter[6,7] applied to gases leads to

$$V_{ng}/V_{air}=\sqrt{\rho_{air}/\rho_{ng}} \tag{3}$$

Using the density of air at 25°C and 1 atm, the density of our natural gas is 0.579 g/L under the same conditions. Methane is usually the major component of natural gas, and its density[8] under the same conditions is 0.657 g/L. Such discrepancies can cause concern, but it should be realized that the composition of natural gas is dependent on its source and upon the life of the well from which it is extracted. For example, the analysis of natural gas from 18 locations[9] in the U.S. yields the following ranges and median values for the following components: CH_4, 98-24%, 85%; C_2H_6, 70-0%, 8%; N_2, 8-0%, 1%; and CO_2, 25-0%, 1%.

Stoichiometry and Material Balances • The emission analyzer provides a measure of the oxygen in the gas sample as a volume fraction; with the ideal-gas assumption, here and throughout, this corresponds to a mole fraction, y_{o_2}. From this measurement, the instrument calculates the volume fraction of carbon dioxide and the fraction of excess air. For the complete combustion of a general hydrocarbon, C_mH_n, in excess air, represented by the stoichiometric coefficient x, the reaction is

$$C_mH_n+\left(\frac{4m+n}{4}+x\right)O_2\rightarrow mCO_2+\frac{n}{2}H_2O+xO_2 \tag{4}$$

The stoichiometry is summarized in Table 1 for various bases, and in Table 2 the corresponding molar flows and mole fractions in the exiting flue gas are listed.

In understanding the operation of the gas analyzer, it is recognized that various quantities are calculated from the measured mole fraction of oxygen; these are the mole fraction of carbon dioxide and the excess air. The basic procedure is to get an expression for the stoichiometric coefficient of excess air, x, in terms of the mole fraction of oxygen (see Table 2, Eqs. T1 and T4). Then the mole fraction of carbon dioxide is calculated (see Table 2, Eq. T3). The fraction of excess air is usually defined[10] by

$$E_{air}=\frac{\begin{pmatrix}\text{moles of}\\ \text{air fed}\end{pmatrix}-\begin{pmatrix}\text{moles of air required}\\ \text{for complete combustion}\end{pmatrix}}{\begin{pmatrix}\text{moles of air required}\\ \text{for complete combustion}\end{pmatrix}}=\frac{4x}{4m+n} \tag{5}$$

To apply the appropriate stoichiometry, two cases under which the analyzer operates are identified. For Case 1, it is recognized that the sample stream passes through a condensate trap at room temperature. When the quantity excess air varies from zero to a value $x = x_{crit}$, the water produced will condense to form liquid; this is treated as vapor and liquid in equilibrium. Then, quantities applicable to the wet-product stoichiometry from Tables 1 and 2 are used. Upon increasing the excess air above x_{crit}, there is no longer sufficient water vapor in the product stream to maintain liquid and vapor in equilibrium; this is Case 2, in which all the products are gaseous, and the gaseous-product stoichiometry is applied.

The value of x_{crit} is calculated by setting the vapor-phase mole fraction of water, on the gaseous-product basis, to its saturation value of

$$y_{H_2O} = (n/2)\left(F_0 / F_T^{gas}\right) = y_{H_2O}^{sat} \tag{6}$$

The solution is

$$x = x_{crit} = \left(\frac{1}{1+r_{N/O}}\right)\left[\frac{n}{2\,y_{H_2O}^{sat}} - m - \frac{n}{2} - \frac{(4m+n)}{4} r_{N/O}\right] \tag{7}$$

If the products from the combustion of methane are passed through the condensate trap at 25°C, the value of x_{crit} is 11.2 mol (corresponding to about 560% excess air). This value is exceeded in the experiments described here.

The dry-product stoichiometry is important for understanding the relationships between quantities measured by the gas analyzer and those measured by the traditional Orsat analysis; the mole fractions of gases in the Orsat analysis are on a dry basis.[1,10] When $x < x_{crit}$, then

$$y_{O_2}(\text{gas analyzer}) = \left(1 - y_{H_2O}^{sat}\right) y_{O_2}(\text{Orsat}) \tag{8}$$

At 25°C, $1 - y_{H_2O}^{sat} \cong 0.97$, so the difference in the mole fractions between the two methods is not great. For the other case, when $x > x_{crit}$

$$y_{O_2}(\text{gas analyzer}) = y_{O_2}(\text{Orsat}) \Big/ \left[1 + \frac{n/2}{q + x\left(1 + r_{N/O}\right)}\right] \tag{9}$$

The quantity q is defined in Table 2. If methane is burned in 600% excess air (just above the critical value), then $y_{O_2}(\text{gas analyzer}) \cong 0.97 y_{O_2}(\text{Orsat})$. As the excess air increases further, the two measures of the mole fraction get closer together.

In principle, the calibration of the rotameter can be used to calculate the molar flow of fuel to the burner if the composition of the natural gas is known. To keep things simple, the natural gas is treated as pure methane, following the usual practice.[10] In this case, the molar flow of methane into the burner at 25°C, as a function of the rotameter setting, is

$$F_0(\text{mol } CH_4 / \text{min}) = \frac{\sqrt{\rho_{air}\rho_{CH_4}}}{16.043} V_{air} = 5.50 \times 10^{-2}\, V_{air}(\text{L/min}) \tag{10}$$

This is used in calculations that follow.

The mole fractions of oxygen and carbon dioxide and the excess air are plotted against the volumetric flow rate of natural gas in Figure 1. As the flow of natural gas to the burner increases, the excess air and the fraction of oxygen decrease while the fraction of carbon dioxide increases with the increasing flow. The largest fraction of carbon dioxide (7%) observed here corresponds to the smallest fraction of excess air (60%). The maximum fraction of carbon dioxide possible is 11.7% and occurs under stoichiometric conditions (no excess air); the student can deduce this from Eq. (T3) in Table 2. The student can calculate the maximum fractions of carbon dioxide possible for other hydrocarbons in a similar way; a standard reference contains the values.[8]

Energy Balance • The first law of thermodynamics for steady-flow systems is applicable. There is no shaft work

TABLE 1
Stoichiometry for the Complete Combustion of a Hydrocarbon

Species	*Molar flow into the burner and the flue*	*Molar flow out of the flue*		
		gaseous-product basis	*dry-product basis*	*with liquid water as product, wet basis*
C_mH_n	F_0	0	0	0
O_2	$\left(\frac{4m+n}{4}+x\right)F_0$	xF_0	xF_0	xF_0
N_2	$\left(\frac{4m+n}{4}+x\right)r_{N/O}F_0$	$\left(\frac{4m+n}{4}+x\right)r_{N/O}F_0$	$\left(\frac{4m+n}{4}+x\right)r_{N/O}F_0$	$\left(\frac{4m+n}{4}+x\right)r_{N/O}F_0$
CO_2	0	mF_0	mF_0	mF_0
H_2O	0	$\frac{n}{2}F_0$	0	$y_{H_2O}^{sat}F_T^{wet}$

1. F_0 is the molar flow of hydrocarbon into the burner.
2. $r_{N/O}$ is the molar ratio of nitrogen to oxygen in air, $r_{N/O} = 79.01/20.99$
3. F_T^{wet} is the total molar flow out of the flue.
4. $y_{H_2O}^{sat}$ is the mole fraction of water in the vapor phase when liquid and vapor are in equilibrium.

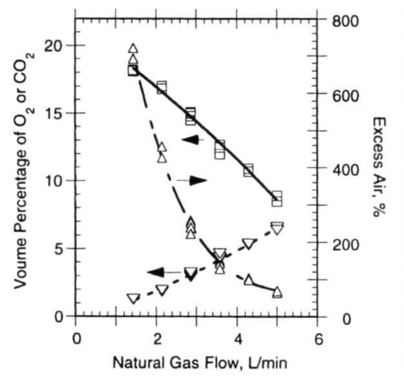

Figure 1. *The measured mole fraction of oxygen (□) in the exiting flue gas as a function of the volumetric flow of natural gas to the burner measured under ambient conditions (25°C, 1 atm). The quantities calculated from measured mole fraction of oxygen are the mole fraction of carbon dioxide (▽) and the percentage of excess air (△).*

and it is assumed that kinetic energy and potential energy effects are negligible.

$$\Delta H = Q \tag{11}$$

The flue pipe is regarded as an open system; ΔH is the enthalpy change from inlet to outlet, and Q is the heat transferred between the system and the surroundings. Because calculation of the adiabatic flame temperature, Q=0, is standard for this system, only the bare details are given here. Many authors[10-14] present methods for calculation of the adiabatic flame temperatures. In calculating them here, the molar heat capacity functions of Smith and coauthors[14] were used, and Visual Basic functions for them within an Excel spreadsheet were written. "Goal Seek" was used to solve for the flame temperatures. The resulting adiabatic flame temperatures and the measured flue gas temperatures are plotted against the volumetric flow rate of natural gas in Figure 2.

The measured flue gas temperatures are used to calculate Q directly; this, the net heat transferred, turns out to be negative as heat is lost from the system, the flame and the flue, to the surroundings. The absolute values of Q as a function of the difference between the temperatures of exiting flue gases and inlet gas temperature (considered to be the same as the surroundings, taken to be 25°C) are plotted in Figure 3. This shows that the rate at which heat is lost from the system increases with this temperature difference in a nonlinear way; this provides an example of the temperature difference as the "driving force" for heat transfer.

Kinetics of NO Formation • Using other electrochemical cells, the analyzer measures volume fractions of nitric oxide, carbon monoxide, and sulfur dioxide. In Figure 4, the levels of nitric oxide and carbon monoxide are shown as a function of the volumetric flow of natural gas; no sulfur dioxide was detected (detection limit ≤ 1 ppm). The level of nitric oxide increases steadily from 6 to 65 ppm with the flow of natural gas; in contrast the level of carbon monoxide starts off at about 17 ppm, decreases to zero and then increases again at the highest flow rate. It is interesting that nitric oxide is

TABLE 2

Molar Flows and Mole Fractions in the Gas Stream Leaving the Flue

Molar Flows

Gaseous-product basis $F_T^{gas} = F_0\left[q + x(1+r_{N/O}) + n/2\right]$

Dry-product basis $F_T^{dry} = F_0\left[q + x(1+r_{N/O})\right]$

Wet-product basis $F_T^{wet} = F_0\left[q + x(1+r_{N/O})\right] / \left(1 - y_{H_2O}^{sat}\right)$

General Expressions for Mole Fractions

$$y_{O_2} = xF_0 / F_T \tag{T1}$$

$$y_{N_2} = \left(\frac{4m+n}{4} + x\right)\frac{F_0}{F_T} r_{N/O} \tag{T2}$$

$$y_{CO_2} = mF_0 / F_T = (m/x) y_{O_2} \tag{T3}$$

Mole Fractions of Water Vapor

Gaseous-product basis $y_{H_2O} = (n/2)F_0 / F_T^{gas}$

Dry-product basis $y_{H_2O} = 0$

Wet-product basis $y_{H_2O} = y_{H_2O}^{sat}$

Expressions for x, the stoichiometric coefficient of excess air, in terms of y_{O_2}

Gaseous-product basis $x = (q + n/2) y_{O_2} / \left[1 - (1 + r_{N/O}) y_{O_2}\right]$

Dry-product basis $x = (q \times y_{O_2}) / \left[1 - (1 + r_{N/O}) y_{O_2}\right]$ [T4]

Wet-product basis $x = (q \times y_{O_2}) / \left[(1 - y_{H_2O}^{sat}) - (1 + r_{N/O}) y_{O_2}\right]$

In the Equations Above $q = m + 0.25(4m+n) r_{N/O}$ and $r_{N/O} = 79.01/20.99$

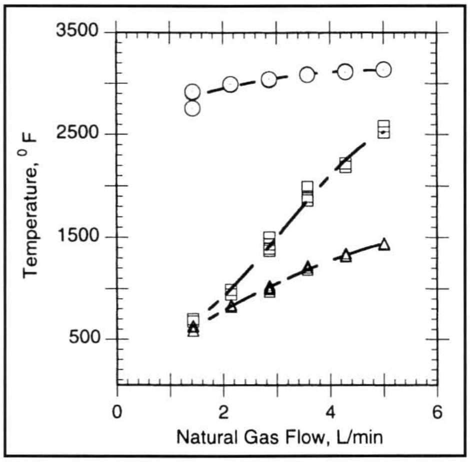

Figure 2. *The measured temperature of the exiting flue gas (△) as a function of the volumetric flow of natural gas to the burner, measured under ambient conditions (25°C, 1 atm). The calculated adiabatic flame temperature (□) and the estimated temperature under which nitric oxide is formed (⊙) are shown.*

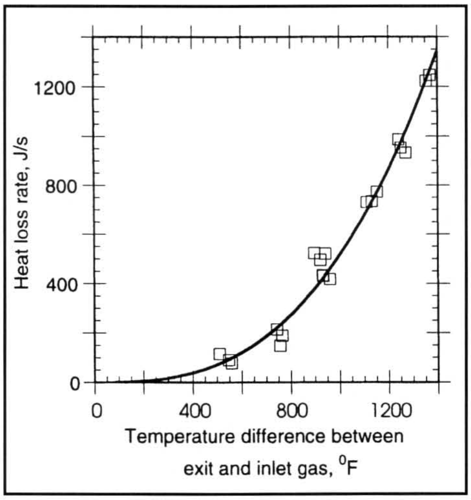

Figure 3. *The heat loss rate from the flue as a function of the difference between the temperatures of the exiting and incoming gases.*

produced in this experiment; this is a major concern in many industrial processes[5,15] because of its potential for release into the atmosphere and its subsequent contribution to the formation of acid rain.

In contrast to the combustion of a hydrocarbon, the formation of nitric oxide from oxygen and nitrogen is endothermic.

$$N_2 + O_2 \Leftrightarrow 2NO \tag{12}$$

Because of this, the formation of nitric oxide is only significant at elevated temperatures. It is instructive to use the known equilibrium and kinetic properties of the reaction to estimate the temperatures that must exist inside the flue. First, the rate of generation of NO within the flue is estimated; then a simplification of the known kinetics is used to estimate the reaction temperature.

The mole fractions of the reactants are about 10,000 times larger than the mole fraction of the product; that is, very little of the reactants is converted to product. So the flame within the flue may be treated as a differential reactor[12,16] running at steady state as far as the formation of nitric oxide is concerned. Under these assumptions, the mole balance leads to

$$F_{NO} - F_{NO,0} - r_{ave} V = 0 \tag{13}$$

where F_{NO} and $F_{NO,0}$ are the molar flows of nitric oxide out and into the flue, respectively, and r_{ave} is the average rate of generation of nitric oxide within the reactor volume, V. It is reasonable to take $F_{NO,0} = 0$, and so

$$r_{ave} = F_{NO} / V \tag{14}$$

The molar flow of nitric oxide out of the reactor is calculated from

$$F_{NO} = y_{NO} F_T^{gas} \tag{15}$$

where y_{NO} is the mole fraction of nitric oxide, the measurement provided by the analyzer, and F_T^{gas} is the total molar flow of gas out of the flue, given in Table 2. Strictly, the molar flow of nitric oxide should be included, but this flow is negligible in comparison to the combined flow of the other species. The effective volume of the reactor is unknown, but the internal volume of the flue available to the flame is about 1 L, and this is used as an approximation for V in the absence of any other information. The estimated rates of generation of nitric oxide are in the range of 0.6-3.0 x 10^{-6} mol $L^{-1}s^{-1}$.

Now an expression for the rate of generation of nitric oxide in terms of the concentrations of the chemical species involved is required. Because of its importance in combustion, the mechanism has received much attention; it is widely believed that the reaction follows the Zeldovich mechanism.[5,17] When this mechanism (under fuel-lean conditions) is applied to our data, it turns out that the forward reaction is dominant; the low levels of nitric oxide seen here are far from equilibrium values, being approximately an order of magnitude smaller than equilibrium values. An abbreviated form of the mechanism that is sufficient to account for the data observed is described; it is also simpler for students, who are encountering mechanisms for the first time, to understand. This abbreviated mechanism is shown in Table 3.

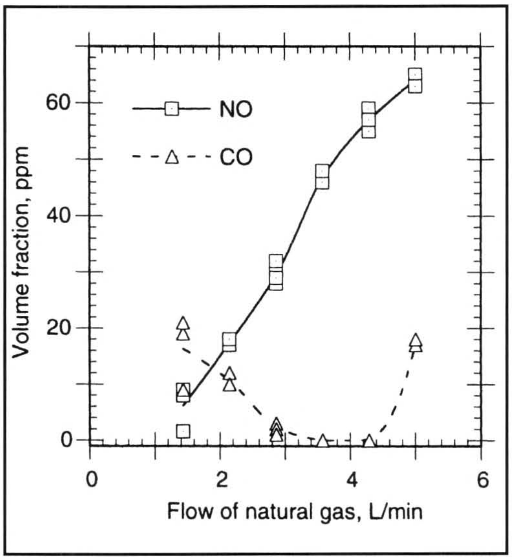

Figure 4. *Mole fractions of nitric oxide and carbon monoxide measured in the exiting flue gas as a function of the volumetric flow of natural gas to the burner, measured under ambient conditions (25°C, 1 atm).*

From the slow steps, the rate of generation of nitric oxide in terms of the concentration of oxygen atoms and concentration of molecular nitrogen is obtained.

$$r = 2k_1[O][N_2] \tag{16}$$

This expression is obtained from the Zeldovich mechanism in the limit of small concentrations of nitric oxide. To evaluate this, the concentration of oxygen atoms in terms of measured quantities is needed. This is a useful exercise in thermodynamics.

$$[O] = [O_2]^{\frac{1}{2}} \left(\frac{P_0}{RT}\right)^{\frac{1}{2}} K_{eq}(T) \tag{17}$$

where P_0 is the standard pressure of 1 bar. Taking the enthalpy for the dissociation of molecular oxygen to be independent of temperature, the van't Hoff equation gives

$$K_{eq}(T) = K_{eq}(T_0) \exp\left[\frac{\Delta H^0}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \tag{18}$$

where $K_{eq}(T_0) = \exp[-\Delta G^0/RT_0]$ and $T_0 = 298$ K. Finally, the gas concentrations in terms of the quanitites measured by the analyzer are required.

$$[O_2] = \frac{y_{O_2} P}{RT} \qquad [N_2] = \frac{y_{N_2} P}{RT} \tag{19}$$

Here, P is the pressure of the reaction, taken to be 1 atm. Table 2, Eq. T2, contains the expression for the mole fraction of nitrogen, y_{N_2}.

The mole fractions in Eq. (19) should strictly be those calculated on the basis of the gaseous-product stoichiometry, as these are the conditions under which the reaction occurs. Most data were obtained under conditions of excess air for which $x < x_{crit}$. So, in principle, the measured mole fractions should be corrected to give the corresponding values on the gaseous-product basis.

$$y_i = y_i(\text{measured for } x < x_{crit})\left(\frac{F_T^{wet}}{F_T^{gas}}\right) \qquad i = NO, O_2, \text{or } N_2 \tag{20}$$

The smallest value of the correction factor is about 0.9; in view of the severe assumption adopted here regarding the reaction volume, the correction is hardly justified.

The reaction temperature is obtained by solving

$$r = r_{ave} \qquad \text{or} \qquad r / r_{ave} = 1 \tag{21}$$

where r and r_{ave} are defined in Eqs. (16) and (14), respectively. This equation was solved using "Goal Seek" within an Excel Spreadsheet. If values of the kinetic parameters typically found in the combustion literature[15,17-19] are used, then the abbreviated mechanism leads to the same results as the full Zeldovich mechanism. But the enthalpy and Gibbs Free energy data were taken from a source to which the student is more likely to have ready access;[20] the temperatures are about 100°F higher with these data, and these higher temperatures are those shown in Figure 2.

TABLE 3
Mechanism for the Formation of NO from O_2 and N_2 in the Initial Stages Under Fuel-Lean Conditions

Step 1	$O_2 \Leftrightarrow O\bullet + \bullet O$	Rapid equilibrium with equilibrium constant K_{eq}
Step 2a	$O\bullet + N_2 \xrightarrow{k_1} N\bullet + NO$	Slow step
Step 2b	$O\bullet + N_2 \xrightarrow{k_1} N\bullet + NO$	Slow step repeated to preserve stoichiometry
Step 3	$N\bullet + \bullet N \rightarrow N_2$	Fast step
Net reaction	$O_2 + N_2 \rightarrow 2\,NO$	
Data (from ref. 17) for	$\frac{1}{2}O_2 \Leftrightarrow O\bullet$	
	$\Delta H^0 = +249.17\ \text{kJ/mol}$	Enthalpy of formation at 298K
	$\Delta G^0 = +231.73\ \text{kJ/mol}$	Gibbs free energy of formation at 298K
Step 2	$k_1 = A\exp(-E_a / RT)$	A=1 x 10^{11} L $mol^{-1}s^{-1}$ E_a = 315 kJ/mol

DISCUSSION

The calibration of the rotameter for the flow of natural gas is useful because it leads the student to an understanding of its principle of operation. The same result can be obtained by asking the student to transform the rotameter's scale from L air/min to L methane/min. The household gas meter used for calibration is a quantity meter; it measures the net volume of gas that passes through it using a displacement method,[6] so its calibration does not depend on the type of gas. To show this, the gas meter was calibrated using the laboratory supply of compressed air, giving

$$V_{air}(\text{gas meter, ft}^3/\text{min}) = (28.3 \pm 0.6)V_{air}(\text{rotameter, L/min})$$
$$r^2 = 0.91 \tag{22}$$

The somewhat low value of the correlation coefficient is attributed to a dirty air supply and the age of the gas meter! But the calibration compares favorably with the conversion, 1 ft^3 ≡ 28.32 L. In contrast, the calibration of the rotameter depends on the density of the gas. By direct calibration of our rotameter, the density of our natural gas was obtained. If the composition of natural gas is known (*e.g.*, by gas chromatography), then the student could be asked to reconcile measured density with the measured composition.

The complete combustion of a hydrocarbon leads to three different ways of expressing the stoichiometry; this may seem strange to the student. This feature arises because of the ways by which the combustion products are analyzed. The traditional Orsat method, providing volume fractions on a dry basis, is specific for O_2, CO_2, and other gases (*e.g.*, CO and H_2). In contrast, our gas analyzer, providing volume fractions on a wet or gaseous-product basis depending on the amount of excess air, is specific for O_2, NO, and SO_2; for the levels of CO_2, the analyzer requires knowledge of the fuel's chemical composition. In environmental applications, it is important to be aware of this feature when attempting to measure levels of CO_2 in situations where the fuel may be inhomogeneous, as in a waste incinerator.

The three bases upon which the stoichiometry is described do not lead to mole fractions that differ by very much in the application considered here. To the practicing engineer, the attention to detail may seem unduly fussy, but it is desirable to train students to formulate a sound theoretical framework from which they can make good practical assumptions and judgements. This is an example of such a process. For whichever basis is appropriate, the mass balance is closed for the primary combustion reaction, assuming it goes to completion. An additional exercise for the student is the explanation of how the molar flow of air into flue varies with the flow of natural gas.

The various temperature data presented here will help the student form a simple picture of a flame, a complicated reacting system.[5] The first observation is that the model to explain the formation of NO leads to temperatures larger than the adiabatic flame temperature, the maximum possible flame temperature, and the measured exit gas temperature. A flame is far from being a homogeneous reaction mixture, either in its temperature distribution or species distribution. The primary reaction, the combustion of a hydrocarbon here, occurs in a zone defined by mixing the fuel and air and their subsequent reaction; this is the so-called combustion zone. Because the combustion is highly exothermic, the heat generated raises the temperature of unreacted gases, such as excess O_2 and N_2, to such a level that they start to react in a zone, the post-combustion zone that is spatially distinct from the combustion zone. Also, it is interesting to note that the NO-formation and adiabatic-flame temperatures appear to converge upon extrapolation to higher natural gas-flow rates where the fuel-air mixture becomes stoichiometric. This suggests that NO is formed in zones within which the local fuel-air mixtures are stoichiometric. So, qualitatively, the first observation can be explained on the basis of reaction zones with non-uniform temperatures and composition.

A second observation supports the idea of non-uniform temperature distribution. After running the experiment at the highest exit temperature (about 1450°F), it was noticed that the burner's nozzle had become partially coated with zinc. This means that the inside wall of the flue must have reached a temperature of 787°F, the melting point of zinc. This is much lower than the NO reaction temperature. The use of a stainless steel flue, or even better a quartz tube, so the structure of the flame can be observed, would be a worthwhile improvement. It would also be safer.

The discrepancy between the adiabatic flame temperature and the exiting gas temperature may seem large. The flue cap used is designed to allow for air infiltration through perforations fabricated in its walls just as the gas leaves the main part of the flue. The astute student will notice this and realize that it will lead to errors in the gas compositions and temperatures; they will be lower than they should be. The cap is designed to ensure a temperature reduction in the gas just before it enters the surroundings. No attempt was made to modify this, or rather to change the position of the probe, because the maximum operating temperature of the probe is 1550°F for continuous service and 2200°F for short-term use. Such imperfections in laboratory experiments, in our opinion, are not a bad thing; they often help students exercise their critical faculties.

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