A Study of Sampling of Flame Gases

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A study of sampling of hot combustion gases by means of water-cooled probes of internal diameter of 0.027 to 0.070 cm has been made. Effect of conditions of sampling on concentrations of CO, CO₂, H₂, and H₂O was the primary interest in this study. The probes were unable to quench reactions completely and were unable to preserve the original composition of the gas, but small probes were more effective than larger probes. Sample composition was unaffected by sampling velocity, except that at the higher rates of sampling it appears that gradients of composition and temperature caused the effectiveness of quenching to decrease. Probe material and configuration had little effect on sample composition.

1. Introduction

The current interest in high-temperature combustion as applied to the field of jet propulsion has led to a need for means to determine the state of the combustion gases in and near the region of chemical reaction. Knowledge of the pressure, temperature, and composition of the gases, among other quantities, is needed to understand the phenomena observed. The composition of the flame gas may be determined by chemical analysis, and temperature, concentration of fuel, and the extent of reaction can be derived. These quantities are determined, of course, for the point or small volume of the engine from which the sample is drawn, and this is one advantage of using chemical analysis.

Samples are commonly taken by drawing the hot gas through tubes that are cooled with water both to protect the tube and to help preserve the composition of the gases being sampled. Chemical analysis will be of value only if the composition of the sample remains unchanged, and this investigation is concerned with the determination of the effectiveness of this method of sampling in preserving the composition of the gas at the point of sampling. The primary interest here is in samples from streams of gas whose compositions are constant at the point of sampling. One requirement of this investigation, therefore, is a source of hot gas whose composition will be constant during the sampling period; a flame burning under controlled steady conditions and of sufficient size relative to the probe and rate of sampling will satisfy this need.

Considerable work which involved sampling and analysis of flame gas was reported during the early years of this century [4 to 16].² Most of this work was done with flames of comparatively low temperature, 1,800° C or less, and the main interest was to determine if chemical equilibrium existed in the flame. Generally, there was no interest in or even recognition of the problems of sampling. Only Haber and Le Rossignol [6] and Haber and Hodsman [7] did any work that involved changing the conditions of sampling. Their method of sampling was to attach an evacuated container to a water-cooled probe and let gas flow in through a stopcock until the pressure reached 0.5 atm. Haber and Le Rossignol used a probe, i.d.=0.015 cm, to sample a carbon monoxide-oxygen flame with a temperature of about 2,900° K. Results of 7 tests, 5 at one rate of sampling and 2 at lower rates, showed some variation of sample composition with rate, but were interpreted to be only a negligible change. The position of the stopcock probably was changed to change the rate of sampling. The speed of the hot gas sample entering the probe at the largest rate of sampling is estimated to be sonic and thus the pressure for this rate is about 0.5 atm at the entrance of the probe. For the lower rates of sampling, the speed and corresponding pressure drop is less. Since the composition of a gas sample in equilibrium is affected by pressure, the composition of the gas sample obtained at the highest rate may have changed more than the others. Haber and Le Rossignol compared the temperature derived from the equilibrium constant for the dissociation of carbon dioxide calculated from the composition of their sample with calculated adiabatic flame temperature, and a concluded that their probe was capable of freezing the dissociation of carbon dioxide and thus of preserving the sample unchanged. But since their method of sampling involves a large pressure change, the effect of the change of pressure on the composition of the sample may have obscured the effect of the probe alone.

Haber and Hodsman used flames of carbon monoxide and oxygen, acetylene and oxygen, and hydrogen and oxygen. Using the hydrogen and oxygen flame, two out of three tests showed a 0.01-cm probe to be more effective than a 0.015-cm probe in freezing the water dissociation, since the temperature based on the water dissociation found in samples taken by the smaller probe was higher than in those taken by the larger probe. As even this higher temperature was about 300° C lower than their calculated flame temperature, they concluded that even the smaller probe could not freeze the water dissociation. Considering the samples drawn from the acetylene-oxygen flames, they concluded that their probes could freeze the carbon dioxide dissociation but not the water dissociation.

¹ This work was sponsored by the Power Plants Division, Bureau of Aeronautics, Department of the Navy. ² Figures in brackets indicate the literature references at the end of this paper.

Erbe, Grey, and Beal [17] sampled a natural gasoxygen flame, and temperatures derived from the values of the equilibrium constants of the products of dissociation of carbon dioxide and water were $2,589^{\circ}$ and $2,644^{\circ}$ K, respectively. They concluded that since these two temperatures were in good agreement their water-cooled probe (internal diameter=0.051 cm) was able to preserve the composition of the flame gas. The given composition of the gas sample can be used to compute the ratio of natural gas to oxygen, and from this ratio, the flame temperature was calculated to be about $2,850^{\circ}$ K. On this basis, their probe did not preserve the composition of the gas in the flame.

It is well known that the composition of a gaseous system in equilibrium can be changed by changing the pressure or by diluting the system with an inert ingredient, provided that the number of molecules of products and reactants are unequal. Hough, Valle-Riestra, and Sage [18] have employed a sampling system in which combustion gas is expanded to a low pressure and simultaneously diluted with helium. Their analytical data indicate the possibility that the reduction of the partial pressure of the components of the sample caused dissociation to overcome the association that would be normal with reduction of temperature only. In this event, apparent quenched temperatures (based on an equilibrium constant derived from the original partial pressures) of the sample would be higher than flame temperature. If a plain water-cooled sampling probe proves inefficient, this procedure of reducing the pressure of the sample may be necessary.

Since previous investigators had paid so little attention to the techniques of sampling, and watercooled sampling probes continued to be widely used, it was decided that a study of sampling hot gases by means of water-cooled probes to determine the effectiveness of this method might prove useful.

The composition of a gas in chemical equilibrium can be determined from a knowledge of the equilibrium constants of the reactions that are taking place. As temperature changes, values of equilibrium constants change, and a sample of gas that is cooled slowly will change in composition down to a temperature T_{q} where the reaction rates are too slow to make any further noticeable change in composition. If gas at temperature T were cooled instantaneously to T_q , then the composition of the gas at T_q would be the same as at T, and the reaction is said to be quenched. In a real case of rapid cooling, as in a sampling probe, equilibrium probably is not maintained and there must be some reaction occurring during the time of cooling down to about temperature T_q . Therefore the gas has a final composition between the initial composition and the composition corresponding to the case of equilibrium cooling. An equilibrium constant based on the final composition and its associated temperature, T_{aq} , may approximate a temperature to which the gas is cooled slowly along an equilibrium path, followed by infinite rate of cooling to stop further reaction. T_{aq} , which may be called an apparent quenched temperature, will approach T only when the degree of conversion of reactants to products is made small by rapid cooling.

Hottel, Williams, and Satterfield [19] have calculated the theoretical composition of flame gas at various temperatures for various burning mixtures based on the assumption that chemical equilibrium exists. Table 1 presents some of their calculated compositions. If a mixture is burned whose theoretical burnt composition is known, and if samples are drawn from the flame and analyzed, we may, by comparing the composition determined by experiment with the theoretical composition, determine T_{aq} for the cooled gas. It is realized that the assumption of chemical equilibrium in flames is questionable. but for the lack of any other data, the values of table 1 are made the basis for comparison. Hottel et al. present the theoretical composition in terms of the molecules H₂, H₂O, N₂, CO, CO₂, and NO, the atoms H and O, and the free radical OH. Of these, H, O, and OH do not exist in the cooled gas, and of

TABLE 1. Equilibrium composition of flame gas according toHottel, et al.

Com-	Percentage present at—									
pound	1,800°K	2,000°K	2,200°K	2,400°K	2,600°K	2,800°K	3,000° K			
	CH4-	$+2O_2$, calc	ulated fla	me tempe	rature=3,	050°K				
HO	0 66440	0 65920	0 6467	0 6216	0 5775	0 5103	0 4109			
H ₂	. 00096	. 00284	. 0069	. 0144	0266	. 0443	. 0662			
Õ	. 00001	. 00005	. 0003	.0014	. 0051	. 0144	. 0338			
H	. 00001	. 00009	. 0005	. 0019	. 0063	.0172	. 0406			
0	00100	00400	0110	0000	0.110	0000	0=00			
O_2	. 00130	. 00426	. 0110	. 0233	. 0413	. 0620	. 0796			
CO	. 00051	. 00201	. 0001	. 0152	. 0310	. 0301	. 0802			
CO	. 00190	. 00009	. 0182	. 0402	. 0/3/	. 1130	. 1490			
CO_2	. 00091	. 92400	. 5105	. 2820	. 2019	. 1021	. 1240			
	CH4+20	$D_2 + 2N_2$, c	alculated	flame ten	perature	=2,800°K				
H_2O	0.39866	0.39559	0.38827	0.37340	0.34719	0.30636				
H_2	. 00070	. 00210	. 00510	. 01071	. 01992	. 03332				
0	. 00000	. 00004	. 00025	. 00115	. 00407	. 01148				
н	. 00001	. 00007	. 00040	. 00104	. 00542	. 01495				
O_2	. 00080	. 00282	. 00725	. 01020	. 02070	. 05940				
OH	. 00035	. 00141	. 00428	. 01059	. 02196	. 03887	198922			
NO	. 00021	. 00068	. 00177	. 00384	. 00709	. 01135	1.0.1			
N_2	. 39944	. 39808	. 39482	. 38831	. 37725	. 36091				
CÓ	. 00140	. 00493	. 01336	. 02925	. 05291	. 08040	1.2.			
CO_2	. 19837	. 19428	. 18450	. 16586	. 13749	. 10290				
	CH ₄ +20	$D_2 + 4N_2$, c	alculated	flame ten	nperature	=2,600°K				
	1	1	1	1	1	1	1			
H_2O	0. 28473	0.28251	0. 27723	0. 26645	0. 24728					
H_2	. 00057	. 00170	. 00413	. 00869	. 01621	N. C. S.				
0	. 00000	. 00003	. 00022	. 00101	. 00356					
H	. 00001	. 00007	. 00036	. 00148	. 00489	1.20.20				
O_2	. 00067	. 00220	. 00563	. 01178	. 02046					
OH	00028	00122	00340	00839	01734					
NO	00028	00072	. 00187	. 00405	00746	1997	1911 1 1 1 1			
N ₂	. 57079	. 56925	. 56554	. 55811	. 54549	1. 1. 1. 1				
CÓ	. 00113	. 00398	. 01074	. 02339	. 04195					
CO_2	. 14160	. 13842	. 13088	. 11665	. 09536	249				
	CH ₄ +20	$_{2}+7.52N_{2}$,	calculate	l 1 flame te	 mperature	e=2,250°K	ι Σ			
	1		1	1		1				
H_2O	0. 18942	0. 18789	0. 18420				1.			
H_2	. 00044	. 00131	. 00320				1233			
H	. 00000	. 00003	. 00019			12.1.1.1.1.1.2.2	-			
O_2	. 00050	. 00163	. 00032		1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.	1				
оп	00001	00004	00957				1.2.1.1			
NO	. 00021	. 00084	. 00207							
NO	. 00021	. 00070	70014							
CO	00088	00307	00824							
co.	00419	00175	00021							
1 1 1 2	11279		. 05015			1	1			

the molecules, H_2 , CO, and CO₂ are most easily determined analytically. In the experimental work to be presented, T_{aq} is determined by comparison of theoretical and experimental mole ratios of CO/CO₂ and H_2/H_2O . By comparing the apparent quenched temperature with the calculated adiabatic flame temperature T, the effectiveness of probes in quenching reactions can be determined qualitatively at least.

Sodium line reversal temperatures for some combustible mixtures are listed in reference [20a]. The calculated adiabatic flame temperatures for some acetylene mixtures are within 100° of the measured temperatures of 2,500° and 3,200° K. The measured temperature of a natural gas flame was 2,200° K, and the calculated temperature was 2,230° K. Some measurements of temperatures of methane flames at the Bureau show similar results. At a sodium line reversal temperature of 2,600° K, the calculated temperature was about 75° higher, whereas at 2,100° K, the measured and calculated temperatures corresponded. Since measured temperatures are close to the calculated equilibrium temperatures, it seems likely that the composition of the flame gas should be close to the calculated equilibrium composition.

2. Apparatus and Analytical Method

Exhaust gas was provided by burning mixtures of methane, air, and oxygen in Bunsen cones at the discharge port of a nozzle. Three different nozzles with port diameters of 1.27, 0.475, and 0.318 cm, respectively, were used in order to keep within the blowoff and flashback limits of the burning mixtures. The burner was mounted horizontally to prevent



water condensing on the probe from falling into the fire.

The rates of flow of methane, oxygen, and air to the burner were controlled and measured in separate systems; each consisted of a pressure-reducing valve, a flow controller, a rotameter, and a manometer. The gases were first dried by passing through activated alumina.

Water-cooled probes, illustrated in figure 1, were used to sample the hot flame gas. Probes of design 1 were constructed of stainless-steel hypodermic needles or of tubing of other metals mounted transversely in a piece of flattened copper tubing. Dimensions of these probes are listed in table 2. Probes

TABLE	2.	Probe	desian	1.	dime	nsions
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\mathbf{D}/\mathbf{A}	Material	Probe						
		А	в	C	D	Е		
21	Stainloss stool	<i>cm</i>	<i>cm</i> 0.051	cm	cm	<i>cm</i>		
33	do	0.027	0.031	.08	1.86	0. 56		
25	do	. 070	. 094	. 11	1.70	. 65		
35	Platinum	. 037	. 135	. 08	1.30	. 43		
39	do	a. 035	. 135	. 08	1.35	. 36		
75	do	. 035	. 135	. 10	2.62	. 75		
39	Silver	. 035	. 135	. 08	1.38	. 46		

a Nozzle inlet diameter 0.060 cm, putlet diameter 0.035 cm, forme d at entrance

of design 2 were made of stainless steel hypodermic needles with a right-angle bend or with a 90° turn, with a radius of $\frac{1}{16}$ in., mounted in thin-walled copper tubing. The bend or turn was set as close as possible to the copper wall and the projecting tip was made less than 1 diameter of the gas passage in length. Probes were mounted with the entrance to the gas passage coaxial with the cone of the flame, and the distance from the cone could be changed by a rack and pinion.

Gas samples were analyzed either gravimetrically, using a combustion train, or volumetrically, using a Shepherd gas-analysis apparatus. The rate of flow of gas through the train was controlled and measured by the exhaust-metering system. The combustion train and exhaust-metering system are illustrated in figure 2, in which A represents a cold trap; B, a



FIGURE 2. Schematic diagram of combustion train and exhaust metering system.

quartz combustion tube packed with copper oxide; C, a flow controller; D, a rotameter and control valve; E, a manometer to measure the pressure in the metering part of the system; F, a bleed valve to control the pressure in the system; 1, a Turner absorption bottle containing in order Drierite and phosphorus pentoxide separated by asbestos; 2 and 4, Turner absorption bottles containing in order Ascarite and phosphorus pentoxide separated by asbestos; and 3, a Turner absorption bottle containing in order Anhydrone and phosphorus pentoxide separated by asbestos. The Turner absorption bottles were modified by fusing male spherical joints to the arms of the caps.

Temperature of the combustion tube was measured by a Chromel-Alumel thermocouple, placed alongside it and shielded from the coils of the furnace by platinum foil.

For gravimetric analysis, gas samples were drawn continuously from the flame through a water-cooled. probe and into the combustion train at a constant specified rate. The pressure in the exhaust-metering system was kept at 20 in. of mercury absolute. The combustion tube was kept at 270° to 295° C, the range in which carbon monoxide and hydrogen are oxidized to carbon dioxide and water respectively. while hydrocarbons are unaffected. Water in the sample was condensed in the cold trap and the remaining traces were removed by the Drierite. Carbon dioxide in the sample was determined by change in weight of the first Ascarite bottle, while carbon monoxide and hydrogen were determined by change in weight of the Ascarite and the Anhydrone bottles, respectively, both after the furnace. Water in the sample was approximated from the total weight of carbon dioxide collected and the carbonhydrogen ratio of methane.

Samples for volumetric analysis were collected by two different methods: (1) By drawing exhaust gas at a measured rate through a sample container and displacing the air, and (2) by the outflow of mercury from the sampling container into a leveling container which was lowered at a constant rate. Method 1 was used only when it was desired to collect a sample for volumetric analysis simultaneously with the operation of the train. The sample container was inserted between the cold trap and the first absorption bottle. Method 2 was used to collect samples for volumetric analysis when the sampling rate was too low to be measured in the exhaust-metering system.

3. Experimental Results

The factors studied in the investigation of quenching of reactions were the velocity of the hot gas in the entrance of the probe, the internal diameter of the gas passage in the probe, the materials of which the gas passage was constructed, and the probe design. Sampling velocity is calculated as follows: It is considered that, since fuel and oxygen are always used in stoichiometric proportions, only the nitrogen supplied in the combustible mixture remains to be

metered in the gas after passing through the combustion train. The theoretical nitrogen content of the burnt gas for a given combustible mixture and given flame temperature is obtained from table 1. The volume of gas entering the probe is calculated from the volume of gas passing through the rotameter of the exhaust-metering system corrected to atmospheric pressure, the theoretical nitrogen content, the ratio of the calculated flame temperature to room temperature, and the measured diameter of the probe.

3.1. Effect of Sampling Velocity and Probe Size

In all of the experiments reported in this section, the burning mixture used had mole proportions $CH_4:O_2:N_2=1:2:2$, and the calculated adiabatic flame temperature of this mixture was 2,800° K. The mixture was burned on the port of a 0.475-cm nozzle and the probe was set 0.36 cm from the tip of the inner cone of the flame. Lewis and Von Elbe [20b] report that the maximum temperature is some distance from the tip of the inner cone. Some tests were made of the variation of apparent quenched temperature with distance from the flame tip, and these showed that the distance chosen, 0.36 cm, was at or near the zone of maximum temperature. A series of experiments was made to discover if the composition of the sample varied with velocity of sampling. Four probes were used in these experiments: A 0.027-cm steel probe, a 0.035-cm platinum probe, a 0.057-cm steel probe, and a 0.070-cm steel probe. Effect of sampling velocity on the composition of the sample, as measured by the mole ratios of carbon monoxide to carbon dioxide and of hydrogen to water, is shown in figures 3 and 4. Table 3 presents some data that was derived from these experiments. The experimental ratio H₂/H₂O is compared with the calculated ratio $H_2/H_2O + \frac{1}{2}H + \frac{1}{2}OH$ because it is considered that H and OH appear as H₂O in the cooled sample.

For all four probes, the ratio CO/CO₂ appears to be constant for a limited range of sampling velocities and then decreases as the velocity of sampling increases. The ratio H₂/H₂O exhibits a similar behavior for three out of four probes, only the curve for the 0.035-cm platinum probe does not show a point of inflection. If the amount of flame gas drawn into the probe is expressed as a fraction of the total mass of the burnt gas, it is found that this fraction is always between 1 and 2 percent at the point of inflection. This suggests that as the rate of sampling is increased beyond this point, gas from cooler regions of the flame is drawn into the probe, causing the values of the ratios to decrease. The sampling velocities at the point of inflection listed in the previous table represent the limit beyond which our samples are no longer representative of the central region being sampled. Under different circumstances, if the gas being sampled contained no fixed temperature and concentration gradients. these points of inflection would not be expected to occur.



FIGURE 3. Effect of rate of sampling on composition.

○, 0.027-cm probe, design 1; •, 0.027-cm probe, design 2; △, 0.035-cm probe, design 1; □, 0.035-cm probe, modified design 1. Numbers near points represent number of experiments averaged to find value plotted.



FIGURE 4. Effect of rate of sampling on composition. \bigcirc , 0.057-cm probe, design 1; \bigcirc , 0.061-cm probe, design 2; \triangle , 0.070-cm probe, design 1.

It will be noted that the highest velocity of sampling in figures 3 and 4 is 70,000 cm/sec. If the velocity were calculated more accurately to take account of compressibility, the velocity would actually be about 92,000 cm/sec, the Mach number would be about 0.85, and the pressure at the entrance of the probe about $\frac{2}{3}$ atm abs. Reynolds number of the flow formed from the internal diameter of the tube, density, velocity of sampling, and viscosity was always below 2,000, and hence if the flow were laminar in the flame, it would remain so in the entrance to the probe. There was some indication with the 0.027-cm probe, at sampling velocities of 2,000 cm/sec and less, that poor quenching was caused by condensation of water in the gas passage. When the flow of cooling water in the probe was reduced until the exit water was about 37° C, quenching was improved. Tests with the larger steel probes at low sampling velocities were not so extensive, and it is possible that some of the low values obtained in the 0.061-cm and 0.070-cm probes could be due to the same cause.

	Carbon				Hydrogen			
Probe size	Maximum CO/CO ₂	Maximum (T ₂ q)co	Sampling velocity at point of inflection	Sampling rate ^a at point of inflection	Maximum H ₂ /H ₂ O	Maximum (T _{eq})H ₂	Sampling velocity at point of inflection	Sampling rate ^a at point of inflection
cm 0. 027 . 035 . 057 . 070	$\begin{array}{c} 0.\ 220 \\ .\ 195 \\ .\ 165 \\ .\ 135 \end{array}$	$^{\circ}$ K 2, 450 2, 420 2, 380 2, 335	<i>cm/sec</i> 30,000 17,000 11,000 7,500	cm ³ /sec 2.3 2.2 3.8 4.1	$\begin{array}{c} 0.\ 010 \\ .\ 008 \\ .\ 006 \\ .\ 005 \end{array}$	$^{\circ}$ K 2, 100 2, 090 2, 040 2, 000	cm/sec 30, 000 10, 000 5, 000	<i>cm</i> ³ / <i>sec</i> 2. 3 3. 5 2. 6

TABLE 3.

^a At room temperature and pressure and wet.



FIGURE 5. Effect of size of probe on apparent quenched temperature.

a, Based on CO/CO_2 ; b, based on H_2/H_2O .

The relation of apparent quenched temperature to the size of the probe is shown in figure 5. It is seen that, both for the data from the CO/CO_2 ratio and the H_2/H_2O ratio, apparent quenched temperature decreases linearly as the diameter of the probe increases. If we extrapolate to zero diameter, the apparent quenched temperature derived from the ratio CO/CO_2 is about 2,520° K, and from the ratio H_2/H_2O , about 2,175° K. These temperatures should be compared with a calculated flame temperature of 2,800° K. Apparently simple convective cooling in the probes is insufficient to preserve the gas sample unchanged, no matter how small the size of the probe. However, if the diameter of the probe is made very small, of the order of the mean free path of the gas molecules, it may be expected that processes other than convective cooling may begin to be effective.

3.2. Probe Materials

Probes with gas passages of stainless steel, platinum, and silver were tested. Effectiveness of quenching was little affected by the material of the probe. Values of the mole ratios of CO/CO_2 and H_2/H_2O obtained with probes of similar size but different materials were similar in magnitude.

Probes with stainless-steel gas passages proved particularly susceptible to corrosion and scaling, especially at the tip of the steel tube. It was suspected that interaction between the steel of the gas passage and the copper of the body was responsible. When the copper body was painted with an aluminum-silica heat-resistant paint, corrosion and scaling stopped. Before this paint was used, probes would clog by accumulation of scale in 10 min or less in some instances, and some probes were destroyed in less than 5 hr of use. After painting, one steel probe was used for 30 hr without any signs of deterioration. Silver probes proved undesirable because in each test the gas passage was constricted by formation of a loose black scale, possibly silver oxide. Platinum probes proved satisfactory; no failures were experienced with three different probes which were used for a total of 60 hr.

3.3. Probe Design

A probe with an internal diameter of 0.035 cm and a ratio of length of gas passage to diameter of 75 to 1 was built and tested. Results obtained with this probe were not significantly different from those obtained previously with a probe of the same diameter, but with a ratio of length of gas passage to diameter of 35 to 1. Therefore a ratio of length to diameter of about 35 to 1 is sufficient to cool the gas.

It was considered that conditions of flow in the entrance to the probe were among the factors that might influence the rate of cooling of the hot gas. In efforts to improve the mixing and rate of cooling. right-angle bends and 90° turns over a radius of 1/16 in. were introduced in the gas passages of two probes. Results obtained with a 0.027-cm probe having a 90° turn are illustrated in figure 3. Some improvement in performance over the straight probe is noted, but not enough to warrant adoption of this feature. Maximum apparent quenched temperature based on the carbon data was about 2,530°K. A 0.061-cm steel probe with a right-angle bend showed no improvement over the 0.057-cm steel probe. Maximum apparent quenched temperature was 2,350°K. Results obtained with the 0.061-cm probe are shown in figure 4.

An entrance nozzle, 0.060 cm in diameter, as illustrated in figure 1, was formed on the tip of a 0.035-cm platinum probe to prevent possible separation of flow and formation of a stagnant boundary layer. Results obtained with this probe are shown in figure 3. Some improvement was found over the plain 0.035-cm probe, but the gain was not outstanding. Maximum apparent quenched temperature was 2,470°K.

3.4. Effect of Temperature of Source of Exhaust Gas

The experimental work described previously was carried out on exhaust gas provided by burning a mixture of methane, air, and oxygen in mole proportions $CH_4:O_2:N_2=1:2:2$. Calculated adiabatic flame temperature was 2,800°K. The apparent quenched temperature based on the mole ratio CO/CO_2 was about 2,420°K when using a 0.035-cm platinum probe, and based on the mole ratio H_2/H_2O was about 2,090°K. It was decided to run a series of tests using flames of different temperatures as the gas sources to determine the variation of apparent quenched temperature with flame temperature. Mixtures with the following mole ratios were used to provide flames with the indicated temperatures:

 $CH_4:O_2=1:2, 3,050^{\circ}K;$ $CH_4:O_2:N_2=1:2:4, 2,600^{\circ}K;$ $CH_4:O_2:N_2=1:2:5.83, 2,400^{\circ}K;$ and $CH_4:O_2:N_2=1:2:7.52, 2,250^{\circ}K.$

All samples were analyzed gravimetrically using the combustion train. Sampling velocity ranged from 5,000 to 30,000 cm/sec, and the same 0.035-cm platinum probe was used.

In the case of the mixture $CH_4:O_2=1:2$, which was burned on a 0.315-cm nozzle, about 8 percent of the total burned gas, as determined from the tables of Hottel, Williams, and Satterfield, would remain after passage through the combustion train. This remainder if metered at the lowest indication of the flowmeter used would correspond to a sampling velocity of 45,000 cm/sec. As it was desired to collect samples at velocities lower than this for the purpose of comparison with previous work, the practice was adopted of bleeding air, dried and freed from CO_2 , into the train after the probe but before the first absorption bottle. By holding a constant flow at the meter and varying the amount of air bled in, the flow in the probe could be changed and estimated.

At a sampling velocity of about 20,000 cm/sec, values of the mole ratio CO/CO_2 varied from 0.13 to 0.25 and the mole ratio H_2/H_2O varied from 0.0039 to 0.0085. Apparent quenched temperatures based on the carbon data ranged from 2,380° to 2,550°K, and based on hydrogen from 1,980° to 2,150°K. Average mole ratio CO/CO_2 was 0.240, which indicates an apparent quenched temperature of 2,530°K; average mole ratio H_2/H_2O was 0.007, which indicates an apparent quenched temperature of 2,090°K. The reason for this poor reproducibility is not known.

For the mixture $CH_4:O_2:N_2=1:2:4$, burned on the 0.475-cm nozzle, the apparent quenched temperature based on the CO/CO_2 ratio, 0.135, was 2,310°K, and that based on the H_2/H_2O ratio, 0.007 was 2,025°K.

For the mixture $CH_4:O_2:N_2=1:2:5.83$, also burned on the 0.475-cm nozzle, the apparent quenched temperature based on the CO/CO_2 mole ratio 0.110 was 2,250°K, and that based on the H_2/H_2O ratio 0.0043 was 1,920°K.

For the mixture $CH_4:O_2:N_2=1:2:7.52$, results were erratic and reproducibility was poor. For samples collected at the same conditions, mole ratio of CO/CO_2 ranged from 0.042 to 0.016 and mole ratio H_2/H_2O from 0.0005 to 0.006. Apparent quenched temperature based on CO/CO_2 ranged from 1,900° to 2,050° K and based on H_2/H_2O from 1,600° to 1,960° K. In these tests the gas velocity was 117 cm/sec at the port of the 1.27-cm nozzle, and the flame was irregular and unstable. The burner was mounted horizontally and the tip of the flame was displaced upward by convection currents. Under these conditions it was difficult to position the probe with respect to the flame. However, one group of tests that gave fairly consistent results indicated an apparent quenched temperature of 2,000° K based on carbon, and of 1,850° K based on hydrogen. The effects of convection were negligible when using burning mixtures with higher flame speeds in the smaller nozzles.

Apparent quenched temperatures based on hydrogen are uniformly lower than those based on carbon. This would indicate, perhaps, that reactions producing water are faster than those producing carbon dioxide and thus cannot be quenched as effectively.

In one series of tests, using the burning mixture $CH_4:O_2:N_2=1:2:2$, samples for volumetric analysis were collected simultaneously with the operation of the combustion train. Apparent quenched temperatures of the cooled gas were determined by the calculation of the mole ratios of CO/CO_2 and H_2/H_2O from both the gravimetric and volumetric analyses and by calculation of the equilibrium constants. from the volumetric analyses, for the reactions $CO_2 \rightleftharpoons CO + \frac{1}{2}O_2$ and $H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$. Agreement was good for the carbon data. Temperatures derived from the equilibrium constants were about 40° C higher than those from the gravimetric mole ration CO/CO_2 . For the hydrogen data, temperature based on the equilibrium constant was about 200° C higher than that based on the gravimetric mole ratio H_2/H_2O . Apparent quenched temperatures based on hydrogen data are always lower than those based on carbon regardless of the basis for determination of temperature.

Apparent quenched temperatures based on the gravimetric mole ratios are plotted against the calculted adiabatic flame temperatures in figure 6.



FIGURE 6. Effect of temperature of gas source on apparent quenched temperature.

Size of circles denote deviation.

The size of the points plotted represents the average deviation of the data. It is seen that the higher the temperature of the gas being sampled, the less effective is the quenching of reactions in a probe. For the gas mixture with a calculated flame temperature of 3,050° K, the apparent quenched temperature based on carbon data was 2,530° K, which is a drop of 520°; for the gas mixture with a calculated flame temperature of $2,250^{\circ}$ K, the apparent quenched temperature based on carbon data was about 2,000° K, which is a drop of 200°. It is apparent also that as the temperature decreases, the difference between temperatures based on CO/CO_2 and H_2/H_2O also decreases. It appears that these two apparent quenched temperatures would become equal at about 1,600° K, and would coincide with the calculated flame temperature. Thus, apparently, a probe should function perfectly at this gas temperature and the composition of the cooled gas should be the same as the composition of the flame gas.

These experiments were made using various mixtures of fuel, oxygen, and nitrogen to change the temperature of the flame gas, and in doing so the composition as well as the temperature of the flame gas was changed. The effects observed may be due in part to this change of composition, but the magnitudes of such effects would be almost impossible to predict. A series of experiments designed to test the effects of concentration probably would give more reliable information, but time for this was not available, and this is left as a possibility for future endeavor. Effects of change of composition should be recognized, however, and an empirical correlation that includes the effects of composition on the sample may be of some value.

The complicated series of reactions that actually take place in the sample tube were simplified for the present purpose, in the case of reactions producing CO_2 , to the reaction

$$2CO+O_2 \rightleftharpoons_{k_2}^{k_1} 2CO_2$$

and this was used as a basis of the empirical correlation. Correlations based on other reactions possibly could serve as well or better, but only a long series of experiments could indicate those that actually control over a wide range of conditions. Rates of reaction are designated by the letter k. The change of concentration (C) of CO₂ due to reaction is

$$\frac{dC_{\rm CO_2}}{dt} = k_1 C_{\rm CO}^2 C_{\rm O_2} - k_2 C_{\rm CO_2}^2,$$

and the change of concentration due to change of sample temperature T in the tube at constant pressure p is

$$\frac{dC_{\rm CO_2}}{dt} = -\frac{p_{\rm CO_2}}{RT^2} \frac{dT}{dt}$$

from differentiation of the gas law, $p_{\rm CO_2} = C_{\rm CO_2} RT$. The total change is the sum of the individual changes, and this leads to

$$\frac{dp_{\mathrm{CO}_2}}{p_{\mathrm{CO}_2}} = \frac{k_1}{(RT)^2} \left[\frac{p_{\mathrm{CO}}^2 p_{\mathrm{O}_2}}{p_{\mathrm{CO}_2}} - \frac{p_{\mathrm{CO}_2}}{K_p} \right] dt$$

after expressing concentration in terms of partial pressure p and using for this reaction the relations $K_c = K_p R T = k_1/k_2$. K is the equilibrium constant, expressed in terms of concentration or partial pressure. The rate of reaction is related to temperature by the empirical Arrhenius equation

$$k \sim e^{-\frac{A}{RT}}$$

where A is an apparent energy of activation. The time rate of change of gas temperature in small tubes under conditions of viscous flow is apparently nearly proportional to T^2 [17], and if this relation and the Arrhenius equation are substituted in the equation for dp/p, we get

$$\frac{dp_{\mathrm{CO}_2}}{p_{\mathrm{CO}_2}} \sim \frac{e^{-\frac{A}{RT}}}{(RT)^2} \left[\frac{p_{\mathrm{CO}}^2 p_{\mathrm{O}_2}}{p_{\mathrm{CO}_2}} - \frac{p_{\mathrm{CO}_2}}{K_p} \right] \frac{dT}{T^2}.$$

This may be integrated to

$$\log \frac{p_2}{p_1} \sim \operatorname{Eff}\left[\frac{p_{\operatorname{Co}}^2 p_{\operatorname{Co}_2}}{p_{\operatorname{Co}_2}} - \frac{p_{\operatorname{Co}_2}}{K_p}\right] \\ \left[e^{-\frac{A}{RT}} \frac{A^2}{(RT)^2} + 2\frac{A}{RT} + 2\right]_{T_1}^{T_2},$$

where the term containing the partial pressures is an effective value over the limits of integration. Subscripts 1 and 2 refer to conditions before and after sampling, respectively. This was used as a basis for the correlation of the experimental data.

The value of A/R was arbitrarily chosen to be 20,000, and this makes $A^2/(RT)^2 \sim A/RT+2$, and hence the latter term was neglected. Also, if the final temperature T_2 where reaction stops is about 1,600° K, then the terms containing T_2 are negligible with respect to those containing T_1 . As a last simplification, the term p_{CO_2}/K_p was omitted, and initial values of partial pressures (from table 1) in the flame gas were used. These reduce the relation to

$$\log \frac{p_2}{p_1} \sim \text{eff} \left[\frac{p_{\text{CO}}^2 p_{\text{O}_2}}{p_{\text{CO}_2}} \right]_1 \left[\frac{e^{-\frac{20,000}}{T_1}}{T_1^2} \right],$$

and it was found that the relation is linear when the partial pressure term is raised to the 0.1 power. This is plotted in figure 7. It must be emphasized that the relative effects of concentration and temperature in this correlation are only estimated, and therefore the correlation must be used with caution in other situations.



FIGURE 7. Effect of initial conditions on change of carbon dioxide during sampling.

 $p = \text{atm}; T = ^{\circ} \text{K}.$

4. Conclusions

Apparent quenched temperatures derived from the observed compositions are always lower than the flame temperatures; this difference amounts to 500° when the flame is at 3,050° K. The difference between apparent quenched temperature and flame temperature becomes less as the flame temperature decreases. Below 2,250° K, the differences are small and composition of the gas sample is close to that of the flame gas.

Rate of sampling exerts little influence on the composition of samples, providing there are no fixed gradients of temperature and composition near the point of sampling.

Design of probes made little difference in the composition of the samples. A ratio of length to diameter of the gas passage of the probe of 35:1 is adequate for cooling. Apparent quenched temperature is affected by the size of the probe, decreasing as the diameter increases.

Effective quenching of reactions in probes in the range of sizes used in this investigation probably requires other means in addition to water-cooling. Sudden expansion to low pressure or dilution with cold inert gas might help to preserve the original composition.

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