

The peculiarity in the c vs. ρ graph (Fig. 2) exhibiting the tendency for c to decrease and finally become negative as the density increases is believed to be related to the similar tendency of ϕ with hydrogen, and both are evidence for the predominance of repulsive forces between molecules at high densities.

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[CONTRIBUTION FROM THE EXPLOSIVES SECTION, PITTSBURGH EXPERIMENT STATION OF THE U. S. BUREAU OF MINES]

FLAME TEMPERATURES OF HYDROCARBON GASES¹

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In a previous report by Loomis and Perrott⁶ methods were described and results given for the flame temperatures of methane, propane, carbon monoxide and natural gas. They tried several methods for measuring the temperatures of stationary flames, details of which are given in the report mentioned. The spectral-line reversal method was finally adopted for the measurement of the flame temperatures of combustible gases, because after the apparatus has been properly calibrated and standardized, a large number of determinations may be made easily, accurately and quickly. This method was first used by Kurlbaum,⁷ subsequently modified by Kurlbaum and Schulze,⁸ and later by Fery.⁹ More recently, Henning and Tingwaldt¹⁰ used the method to measure the maximum temperature of the acetylene-oxygen flame, 3100°. Griffiths and Awbery¹¹ have also described this method and investigated its limitations and factors affecting the accuracy of the results obtained. Tests made by them to determine the influence of flame thickness on the observed flame temperatures showed that within the limits of 1/2 inch to 2 inches, thickness is immaterial to the result, but to ensure sensitivity it is advisable to employ a thick flame. They also investigated the distribution of temperature from base to tip of the flame. The results showed a relatively uniform temperature

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⁶ A. G. Loomis and G. St. J. Perrott, *Ind. Eng. Chem.*, **20**, 1004 (1928).

⁷ Kurlbaum, *Physik. Z.*, **3**, 332 (1902).

⁸ Kurlbaum and Schulze, *Ber. deut. phys. Ges.*, **5**, 428 (1903).

⁹ Fery, *Compt. rend.*, **137**, 909 (1903).

¹⁰ Henning and Tingwaldt, *Z. Physik*, **48**, 805 (1928).

¹¹ E. Griffiths and J. H. Awbery, *Proc. Roy. Soc. (London)*, **A123**, 401 (1929)

in the lower region of the flame, followed by a very rapid decrease from this zone of uniform temperature as the tip of the flame is approached. They used this method for determining the maximum temperatures in gaseous explosions, for the measurement of the temperatures of stationary flames, using carbon monoxide and air at various ratios and rates, also for the measurement of the temperatures of flames of atomic hydrogen. It is of interest to note that values for the maximum flame temperatures of carbon monoxide-air mixtures varied over a range of 100° with the quantity of mixture burned in a given interval of time. The larger the quantity burned the higher the flame temperature for a given air-gas ratio at a given distance above the burner port. This is equivalent to lowering the point of measurement while keeping the rate constant. The temperatures found at the higher rates appear to approach a constant value. It is, therefore, necessary to burn a sufficient quantity of gas in unit time to ensure measuring the maximum temperature at a given constant distance above the burner.

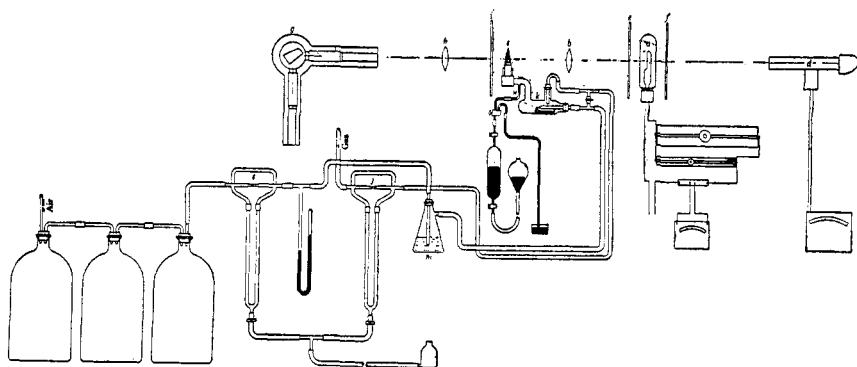


Fig. 1.—Apparatus for determining flame temperatures of gases.

In the spectral-line reversal method employed for obtaining the temperatures given in this report, use was made of a tungsten band lamp as a source of continuous radiation. Figure 1 is a diagrammatic sketch of the apparatus. The tungsten band lamp *a* was heated by a storage battery, the current input being controlled by variable resistances. Light from the band lamp was focused by means of the lens *b* into the center of the flame *c* just above the tips of the inner cones. The brightness temperature of the band lamp was read by means of the optical pyrometer *d*, of the disappearing filament type, the screens *e* and *f* permitting radiation to emerge from the same point on the heated band. The optical pyrometer recorded the same temperature (within 5°) on both sides of the band lamp. Furthermore, there was no evidence of a temperature gradient one centimeter either side of the center of the band. The image of the heated tungsten band together with the flame was focused on the slit of the spectrometer *g* by means of the lens *h*. A screen *i* permitted radiation from an area of the flame equal to the area of the band image to reach the spectrometer. The flame was colored by means of sodium, lithium, or thallium salts. The spectral lines (for sodium, the resonance doublet $\lambda\lambda = 0.5890-0.5896\mu$) are seen as bright lines upon the continuous spectrum from the band lamp if the latter is cooler than the flame, but if it is hotter the bright lines are reversed and appear dark upon the brighter background of the continuous spectrum of the

band lamp. Final adjustment was made by the observer at the eyepiece of the spectrometer. When the lines are just completely reversed the brightness temperature of the tungsten band lamp is the same as the temperature of the flame. At this point the former temperature was determined by means of the optical pyrometer.

Experimental Part

Burners Used in Investigation.—Three types of burners were used in our investigation. These are shown in Fig. 2. Type A consisted of a small brass box 5.5 by 3.5 by 3.5 cm. Protruding through the top of the box were fifteen quartz tubes arranged in three rows, each having an internal diameter of 5 mm. Holes were drilled into the top plate of the box to admit the lower ends of the tubes, which were sealed in gas-tight with sealing wax. Asbestos paper was wrapped around the tubes as shown to prevent the infiltration of secondary air; they were also sealed with wax along the bottom and edges.

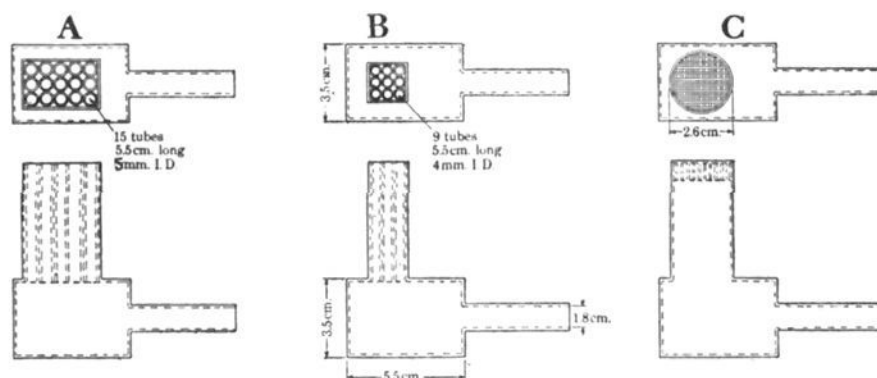


Fig. 2.—Gas burners.

This burner could not be used with some of the unsaturated hydrocarbon gases, which have rather high flame speeds, due to the flames "flashing back" through the tubes. To handle these gases, type B was prepared similar to the foregoing with the exception that there were nine quartz tubes with an internal diameter of 4 mm. In some cases, even with this burner, it was very difficult to obtain satisfactory flames when the mixture contained oxygen in excess of that required for complete combustion. The flames tended to rise or "float" above the burners, or "flash-back" through the tubes.

Finally, a third burner of the Méker type was prepared. This was made as shown in C. The burner head was 2.6 cm. in diameter and was provided with a nickel grid. Flash-backs were further prevented by installing 40-mesh nichrome screens both above and below the nickel grid when necessary.

Regulation of Flames.—The quantity of gas-air mixture was always regulated so that the inner cones remained close to the top of the burner ports. The quantity was then further regulated to give a rather bulky flame which spread out in cross-sectional area equal to the area of the burner ports. Consistent results were possible with any of the burners at a given gas-air ratio, provided that this condition obtained (see results shown in Fig. 4). If the flames tapered off toward the center as they left the burner ports, due to an insufficient amount of mixture being burned, low values were obtained. With some of the mixtures the metal Méker type burner tended to heat up slightly during use; therefore, it was necessary to surround the burner with a thick felt pad which was kept moistened with water. This does not seriously affect the temperature of the flame since any temperature lowering due to heating the burner is practically compensated by the increased temperature due to preheating the incoming gas, barring small losses by convection to the outside atmosphere.

Determination of Gas-Air Ratios.—The combustible gases were admitted to the apparatus either from a 12-cu. ft. gasholder or, in the case of the compressed gases, from tanks through a reducing valve. The quantity of gas admitted was determined by a calibrated flowmeter *j* (Fig. 1) from which the gas passed to the mixing chamber *k*. The air supply was forced through the apparatus by a Lehman rotary pump, having a by-pass arrangement whereby the air pressure could be maintained at any desired value. This regulation was obtained by a fine adjusting needle-valve. The air was then passed through three large stabilizing bottles, through the calibrated flowmeter *l*, a mercury pressure gage, a humidifier *m*, and thence through the atomizer in mixing chamber *k*, whence the gas-air mixture passed directly to the burner *c*. Samples of the gas-air mixtures were taken at *n* by mercury displacement. A small fraction of the sample collected was passed into a collecting tube, and the samples were analyzed in a Bone and Wheeler gas-analysis apparatus.

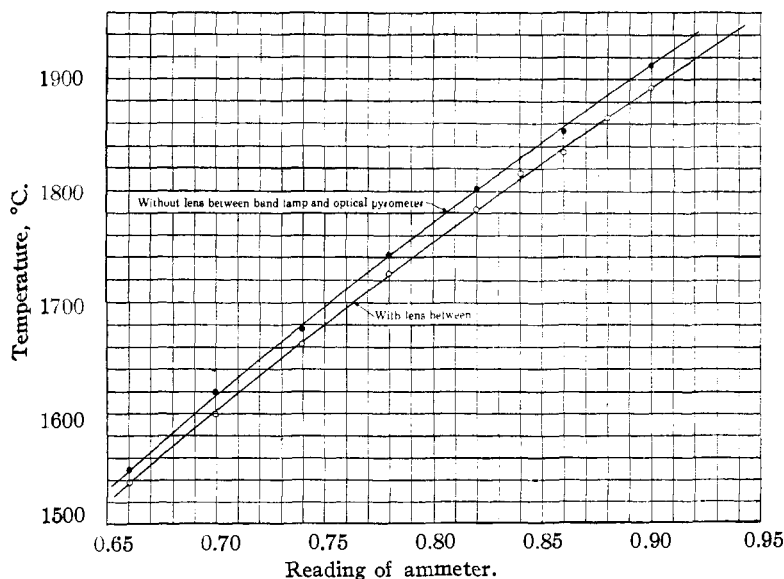


Fig. 3.—Calibration curve for tungsten band lamp and lens.

Calibration of Band Lamps.—General Electric 20-ampere type 4-T-20 tungsten band lamps were used as continuous radiators. Two different lamps were employed during the investigation. Experience with these band lamps showed that the brightness temperature for a given current consumption remained practically constant over long periods. In the preliminary work the brightness temperature of the band lamp was read with an optical pyrometer each time an observation was made. However, by calibrating the band lamp with a calibrated optical pyrometer in which brightness temperature is plotted versus current, the time required to make observations was greatly reduced without sacrificing accuracy. The band lamps were calibrated by H. K. Griffin of the Physical Instruments Calibration Section of the Bureau of Mines and a typical calibration is given in Fig. 3.

Calibration of Lens Correction.—As the radiation from the band lamp passes through a lens before being focused on the flame under investigation, a correction must be applied for the radiation absorbed by this lens. The correction is negative, because, with the

lens absorbing radiation, the lamp must be heated that much hotter before reversal takes place. The values for lens correction are given in Fig. 3. Over the range investigated it varies from 11 at 1600° to 21 at 1950°.

Color Correction.—Tests were made in which the flames were colored with sodium and lithium salts, supplemented by a few tests with thallium salts. As the brightness temperature of the band lamp is measured in the red (λ 0.665 μ) and the temperature of the flame in the yellow (sodium salts, λ 0.589 μ), red (lithium salts, λ 0.671 μ) or green (thallium salts, λ 0.535 μ) a color correction is necessary.

The correction for sodium is determined in the following manner. The relation between the true temperature T and the brightness temperature S_λ as derived from Wien's equation, is

$$\frac{1}{T} - \frac{1}{S_\lambda} = \frac{\lambda 2.303 \log e_\lambda}{C_2} \quad (1)$$

and

$$\frac{1}{T} - \frac{1}{S_{\lambda'}} = \frac{\lambda' 2.303 \log e_{\lambda'}}{C_2} \quad (2)$$

where T is black body temperature in absolute degrees; $\lambda = 0.665\mu$ (red light) or 0.000665 cm.; $\lambda' = 0.589\mu$ (yellow light) or 0.000589 cm.; e_λ and $e_{\lambda'}$ are spectral emissivities of red and yellow light; C_2 is 1.433 cm. degrees; S_λ is brightness temperature as observed with pyrometer; and $S_{\lambda'}$ is flame temperature (brightness temperature of yellow light). By subtracting Equation 2 from 1 we obtain

$$\frac{1}{S_{\lambda'}} = \frac{2.303}{C_2} [\lambda \log e_\lambda - \lambda' \log e_{\lambda'}] + \frac{1}{S_\lambda} \quad (3)$$

Data for the spectral emissivities of tungsten as a function of the true and brightness temperature were obtained from Forsythe and Worthing.¹²

From the curves obtained by plotting μ against the spectral emissivity for different temperatures the spectral emissivity for any wave length can be read off for that temperature. Table I was constructed for the temperature range of these experiments.

TABLE I

SPECTRAL EMISSIVITIES FOR SEVERAL TEMPERATURES AT VARIOUS WAVE LENGTHS

True or black body temp., °K.	Brightness temp. in red, °K.	Spectral emissivity			
		0.665 μ	0.589 μ	0.671 μ	0.535 μ
2100	1943	0.433	0.446	0.432	0.455
2200	2026	.431	.444	.430	.454
2400	2192	.427	.441	.426	.451
2500	2274	.425	.439	.424	.449

From Equation 3 at 1943°K. (in red), a corresponding temperature in the yellow is calculated. $S_{\lambda'} = 1965^\circ\text{K.}$ or 22° higher in the yellow than

¹² Forsythe and Worthing, *Astrophys. J.*, 61, 146 (1925).

in the red. Table II contains the color corrections for sodium and lithium¹³ over a range of temperatures.

TABLE II
COLOR CORRECTIONS

Temp., °K.	Sodium λ 0.589μ	Lithium λ 0.671μ
1943	+22	-2
2026	+23	-2
2192	+28	-2
2274	+30	-3

To check the accuracy of the calculated color corrections, saturated solutions of sodium and lithium nitrates were used in the atomizer. The flame temperatures were observed with ethane-air mixtures, the air-gas ratios being adjusted to give maximum values. Four different tests were made and the following results obtained.

TABLE III
COMPARISON OF SODIUM AND LITHIUM FOR OBTAINING TRUE FLAME TEMPERATURES

Test	Observed temperature, °C.		True corrected flame temperature, °C.		Dif- ference
	Using sodium line	Using lithium line	Sodium +26	Lithium -2	
1	1861	1888	1887	1886	- 1
2	1857	1893	1883	1891	+ 8
3	1870	1888	1896	1886	-10
4	1857	1878	1883	1876	- 7

In every case the observed temperatures for lithium salts are higher than those for sodium salts. When corrections are made for color, as previously described, the flame temperatures for both salts show fairly close agreement.

Introduction of Alkali Salts into Flame.—Both dry and wet methods were used to introduce sodium salts into the flames. In the dry method the air was passed through a quartz tube in which were placed three aluminum boats containing the sodium salts. The quartz tube was heated in an electric furnace to a temperature sufficient to vaporize the sodium chloride in amounts which would produce a good reversal of the sodium lines in the spectrometer. The sodium chloride entered the burner in the form of a cloud. The air in these tests was not humidified before passing through the furnace, the moisture content being that of the laboratory air used. Considerable difficulty was experienced in maintaining a steady concentration of sodium in the flame, and it was necessary to cool the air back to

¹³ The reversal of the red lithium line was not as satisfactory as the sodium line. However, it could be employed by adjusting to the point of extinction. With the thallium line, however, it was impossible to obtain a reversal and the point of extinction was very indefinite. Flame temperatures obtained with thallium salts ranged from 100 to 140° below those obtained with sodium or lithium salts. The use of thallium salts is therefore impracticable.

room temperature by passing it through a lead coil immersed in cold water before mixing it with the combustible gas.

A wet method was finally adopted in which a saturated solution of sodium or lithium nitrate was placed in the atomizer chamber *k* and the salt solution atomized directly into the gas-air mixture. In the wet method the humidifier *m* was used to prevent the salt solution from crystallizing out on the nozzle of the atomizer and causing fluctuations in the rate of flow of air.

The cooling effect of the salt-solution spray was found experimentally by inserting a platinum strip in the non-luminous flame and reading its temperature with an optical pyrometer, with and without pure water being sprayed at the same rate as used in the measurements with the flames. The amount of cooling was found to be 15° for the hydrocarbon flames.¹⁴

A further series of tests was made with Pittsburgh natural gas-air mixtures in the ratios to give approximately maximum flame temperatures (1870 to 1890°) using both the wet and dry methods. In each case where the gas composition was the same the dry method gave higher results which varied over a rather wide range from 4 to 26° . These results appear to show that a correction for water spray is necessary. As an average value a plus correction of 15° has been added to all the results given in this report in which the wet method was used. The cooling effect of salt in the spray has been shown to be negligible.⁷

Gases.—Methane was obtained from a natural gas well near Pittsburgh, Pa. Previous tests of the gas from this well showed the combustibles to consist largely of methane. The gas from the well was compressed in steel cylinders by means of a portable compressor.

The natural gas was that supplied at the Pittsburgh Experiment Station, Bureau of Mines, and varies only slightly from day to day.

The ethane, propane, butane, isobutane, ethylene and butylene were all obtained from the Carbide and Chemicals Corporation of New York in steel tanks.

The propylene was obtained from the Ohio Chemical and Manufacturing Company of Cleveland, Ohio. This gas also was supplied in steel tanks.

A fractionation analysis of each of these gases was made at low temperatures and pressures, using a Shepherd and Porter apparatus for the fractionation and a Bone and Wheeler apparatus for the purity of the fraction. The results of these analyses are given in Table IV. All the gases indicate a small percentage of nitrogen. The high degrees of purity of the propane, butanes and butylene agree well with the specifications for these gases. Percentages less than 0.01% are not recorded. The usual combustion

¹⁴ The laboratory air was nearly always saturated with moisture so that the cooling effect observed is, in a large measure, due to droplets or a cloud of water picked up in the spray.

analyses in a gas-analysis apparatus give only the percentages of hydrocarbon gases in the gas-air mixtures on a dry basis, so that the percentages of gas given in the results described later are on a nitrogen and moisture-free basis.

TABLE IV
COMPOSITION OF GASES USED IN TESTS

Gas	Composition, per cent. by volume							N ₂
	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₂ H ₄	C ₃ H ₆	C ₄ H ₈	
Methane	97.8	1.4	0.1	0.1	0.6
Natural gas	86.6	7.9	2.7	1.3	1.5
Ethane	8.4	89.4	0.4	1.8
Propane	0.0	0.0	99.0	0.0	1.0
Butane	.0	.0	0.0	98.5	1.5
Isobutane	.0	.0	.0	99.5	0.5
Ethylene	1.0	1.5	.2	0.0	96.67
Propylene5	..	3.5	93.3	1.1	1.6
Butylene	0.0	99.9	0.1

Experimental Results

The values found for the flame temperatures of methane, Pittsburgh natural gas, ethane, propane, butane, isobutane, ethylene, propylene and butylene when mixed with varying proportions of air are given in Fig. 4.

Vertical lines are drawn in the graphs representing the composition of the mixture to give complete combustion—that is, just sufficient combustible present to consume all the oxygen in the mixture. A shaded section is also drawn in each graph to show the range in percentage of combustible which has the maximum speed of uniform movement of flame. These values were taken from reports by Wheeler, Coward, Payman and others and represent the speed as measured in a 25-mm. tube for horizontal propagation of flame.

TABLE V

MAXIMUM FLAME TEMPERATURES OF HYDROCARBON GASES WHEN MIXED WITH AIR AND A COMPARISON OF THESE VALUES WITH THE MAXIMUM SPEED OF UNIFORM MOVEMENT OF FLAME

Hydrocarbon	Obs. max. flame temp., °C.	Combustible in air at maximum flame temp., %	Combustible in air necessary to give complete combustion, %	Max. speed of uniform movement of flame, cm./sec.	Combustible in air at max. speed of uniform movement of flame, %	Calcd. max. flame temp., °C.
Ethylene	1975	6.65- 7.00	6.50	165	7.30- 7.70	2072
Propylene	1935	4.45- 4.90	4.45	100	5.00- 5.40	2050
Butylene	1930	3.35- 3.45	3.35	97	3.90- 4.10	2033
Propane	1925	4.05- 4.30	4.00	82	4.60- 4.80	1967
Isobutane	1900	3.15- 3.25	3.10	1973
Butane	1895	3.15- 3.40	3.10	83	3.60- 3.80	
Ethane	1895	5.70- 5.95	5.65	86	6.30- 6.60	1949
Pittsburgh natural gas	1890	8.60- 9.10	8.60	71	9.10- 9.40	1928
Methane	1880	9.45-10.10	9.45	67	9.70-10.00	1918

The variation in the flame temperature given represents the reproducibility that may be expected by this method. In obtaining these temperatures, four different investigators worked on the problem at one time or another, two different tungsten band lamps were used, three different burners, both sodium and lithium salts, and both the wet and dry method of introducing the salts. The values found when using the different burners are properly noted in Fig. 4. They include corrections for water spray, color and lens, as given above. Table V contains a summary of results.

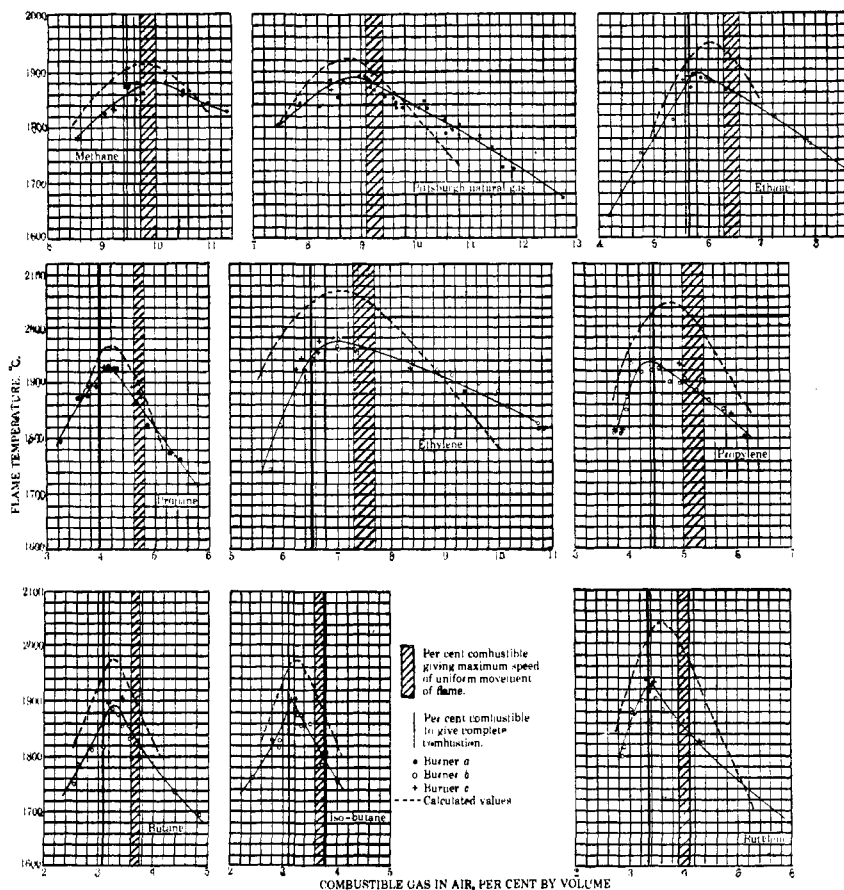


Fig. 4.—Flame temperatures of hydrocarbon gases.

Conclusions

The following conclusions may be drawn. 1. As would be anticipated, the flame temperature is markedly affected by the proportion of combustible gas in air. The flame temperature increases rapidly, starting with a mixture near the lower limit of inflammability and reaches a maximum

when the mixture contains combustible slightly in excess of that necessary to consume all the oxygen present. The reason for this slight shift from a stoichiometric mixture lies in the dissociation of the products of combustion at the high temperatures developed. This is borne out by the calculated temperatures, whose maxima, allowing for dissociation, agree well with the observed maxima (refer to Fig. 4). With further increases in percentage of combustible the flame temperature falls again, although not as sharply as for the mixtures containing excess oxygen.

2. The maximum flame temperatures of the gases tested vary from 1880° for methane to 1975° for ethylene; the maximum variation among the different hydrocarbons is less than 100°.

3. The maximum flame temperatures of the unsaturated hydrocarbons are greater than those of the saturated hydrocarbons.

4. In most cases the maximum flame temperature occurs over a very narrow range of gas-air ratios; a slight change in the gas-air ratio at the maximum causes a sharp reduction in the flame temperature. This is especially true for propane, propylene, butane, isobutane and butylene and not so marked for methane, Pittsburgh natural gas, and ethylene.

5. The combustible gas-air mixture which gives the highest flame temperature does not correspond to that which gives the highest speed of uniform movement of flame, except for methane and possibly Pittsburgh natural gas. For all the other hydrocarbon gases the mixtures which give the highest flame temperatures contain less combustible gas than those which give the highest speed of flame.

6. There is a general agreement between the maximum flame temperatures and maximum flame speeds (Table V). Ethylene has the highest maximum speed of uniform movement of flame and also the highest flame temperature. The others are, on the whole, in the proper order in this respect. The variations as between propane, butane, and ethane are too small to draw significant conclusions. The reason for the non-coincidence of the mixtures which give maximum flame speeds and the maximum flame temperatures is not clear. It has been suggested that the maximum flame temperature may have little or nothing to do with the maximum flame speed but that some lower temperature at which the combustion reaches a certain rapidity may be of importance. In spite of the above-mentioned agreement this may well bear further investigation.

An explanation has been advanced by Payman and Wheeler^{14a} to account for the disagreement between the maximum flame speed mixture and the stoichiometric mixture. According to them the displacement is due to a mass-action effect whose theoretical maximum occurs on the rich side. On the other hand, the highest calorific effect is produced by a stoichio-

^{14a} W. Payman and R. V. Wheeler, "Flame Speeds and Their Calculation," Reprinted from *Fuel in Science and Practice*, 153 (1929).

metric mixture. This factor will oppose the mass-action effect and will diminish the displacement of the maximum speed mixture caused by the latter. It is found that the temperature factor far outweighs the mass-action factor. The resultant displacement will be governed by the cooling effect of the excess combustible gas; the higher the specific heat of the latter at the temperature developed, the less the displacement will be. The displacement for propane and butane should therefore be less than for methane. Actually, it is slightly greater for propane, whereas for butane it is approximately the same as for methane. For ethylene, whose specific heat may also be expected to exceed that of methane, the displacement is twice as great.

Calculation of Flame Temperatures.—We have attempted to calculate the temperatures attained by the flame for the several mixtures used in this investigation. The agreements with the experimental flame temperatures are, in general, so satisfactory as to justify a brief account of these calculations.

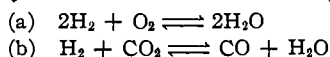
In making the calculations the following assumptions have been made.

1. The initial mixture consists of hydrocarbon gas and air in any desired proportions.

2. The analyses given in Table IV are used for Pittsburgh natural gas and ethane. All other hydrocarbons are considered pure because the small amounts of impurities present introduce only very slight alterations in the final result.

3. The products of combustion consist of carbon dioxide, carbon monoxide, water, hydrogen, oxygen, nitrogen and no hydrocarbons.

4. The products of combustion are in chemical equilibrium at the temperature attained by the combustion. The equilibria considered are



5. The maximum temperature is reached when the products mixture attains the equilibrium condition. This assumption is not an unreasonable one when the combustion is very rapid.

6. The combustion takes place at constant pressure and one atmosphere.

7. The initial temperature $T_1 = 291^\circ\text{K}$., and the final temperature T_2 is the flame temperature sought.

8. The gases are saturated with water vapor at the temperature of the laboratory before being burned.

9. No heat is lost by radiation or conduction.

Method.—In general, the method employed is that used by Goodenough and Felbeck.¹⁵ The following procedure was used.

¹⁵ G. A. Goodenough and G. T. Felbeck, *Bull. Univ. Ill. Eng. Exp. Station*, No. 139, March, 1924.

Initial mixture	Final mixture
1 $\text{CaH}_{2b} = 1$ mole	1 $\text{CO}_2 = ax$ moles
2 $\text{O}_2 = c$ moles	2 $\text{H}_2\text{O} = (b + e)y$ moles
3 $\text{N}_2 = d$ moles	3 $\text{CO} = a(1 - x)$ moles
4 $\text{H}_2\text{O} = e$ moles	4 $\text{H}_2 = (b + e)(1 - y)$ moles
	5 $\text{O}_2 = c + \frac{e}{2} - \frac{a}{2} - \frac{ax}{2} - (b + e)\frac{y}{2}$ moles
	6 $\text{N}_2 = d$ moles
Total moles = $m = b + c + d + \frac{a}{2} + \frac{3}{2}e - \frac{ax}{2} - (b + e)\frac{y}{2}$	

The number of moles of carbon, oxygen, and hydrogen should check in the initial and final mixture. x = fraction of carbon dioxide undissociated in the equilibrium mixture; y = fraction of water undissociated in the equilibrium mixture.

There are three unknowns—namely x , y , and T_2 —and there must be three independent equations from which to determine them. Two are derived from the equilibria mentioned above and the third is obtained by applying the energy equation to the combustion process.

The equations expressing these equilibria are

$$K_{p_{\text{H}_2\text{O}}} = \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2} \sqrt{p_{\text{O}_2}}} = \frac{y}{1 - y} \sqrt{\frac{m}{P \left(c + \frac{e}{2} - \frac{a}{2} - \frac{ax}{2} - (b + e)\frac{y}{2} \right)}}$$

Placing $P = 1$

$$\log K_{p_{\text{H}_2\text{O}}} = \frac{1}{2} \log m + \log \frac{y}{1 - y} - \frac{1}{2} \log \left(c + \frac{e}{2} - \frac{a}{2} - \frac{ax}{2} - (b + e)\frac{y}{2} \right) \quad (1)$$

$$K_{p_{\text{wg}}} = \frac{p_{\text{CO}} p_{\text{H}_2\text{O}}}{p_{\text{CO}_2} p_{\text{H}_2}} = \frac{a(1 - x)(b + e)y}{ax(b + e)(1 - y)} = \frac{y(1 - x)}{x(1 - y)} \quad (2)$$

$K_{p_{\text{H}_2\text{O}}}$ and $K_{p_{\text{wg}}}$ are the equilibrium constants at constant pressure of the water formation and water-gas reactions.

In deriving the energy equation we apply the first law of thermodynamics and assume that no heat is lost in the combustion process. The following series of changes is assumed in passing from the initial to the final state. The mixture is completely burned at the constant initial temperature T_1 ; the products, carbon dioxide and water dissociate at the same T_1 until the composition of the mixture is the same as that in the final state of equilibrium; the final mixture at T_1 is heated without change of composition to the final temperature T_2 .

The energy equation may be expressed as follows: heat of combustion of hydrocarbon = energy required to dissociate carbon dioxide and water + heat capacity of the final mixture from T_1 to T_2 . The final equation is

$$H_{\text{HC}} = aH_{\text{CO}_2} - axH_{\text{CO}_2} + (b + e)H_{\text{H}_2\text{O}} - (b + e)yH_{\text{H}_2\text{O}} + ax \int_{291}^{T_2} C_{p_{\text{CO}_2}} dt \\ + (b + e)y \int_{291}^{T_2} C_{p_{\text{H}_2\text{O}}} dt + a(1 - x) \int_{291}^{T_2} C_{p_{\text{CO}}} dt +$$

$$(b + e) (1 - y) \int_{291}^{T_1} C_{p_{H_2}} dt + \left(c + \frac{e}{2} - \frac{a}{2} - \frac{ax}{2} - (b + e) \frac{y}{2} \right) \int_{291}^{T_1} C_{p_{O_2}} dt + \int_{291}^{T_1} C_{p_{N_2}} dt$$

This can be represented by a linear equation of the type

$$Ax + By = C \tag{3}$$

where

$$A = a \left[\int_{291}^{T_2} C_{p(CO_2 - CO - 1/2 O_2)} dt - H_{CO_2} \right]$$

$$B = (b + e) \left[\int_{291}^{T_1} C_{p(H_2O - H_2 - 1/2 O_2)} dt - H_{H_2O} \right]$$

$$C = H_{HC} - aH_{CO_2} - (b + e) H_{H_2O} - \left(\frac{a}{2} + \frac{e}{2} + c + d \right) \int_{291}^{T_2} C_{p_{O_2 \text{ or } N_2 \text{ or } CO}} dt - (b + e) \int_{291}^{T_1} C_{p_{H_2}} dt.$$

H_{HC} = heat of combustion of hydrocarbon gas

H_{CO_2} = energy to dissociate one mole of CO_2 to CO and O_2

H_{H_2O} = energy to dissociate one mole of H_2O to H_2 and O_2

By eliminating y in (2) and (3) a quadratic equation in x is obtained

$$A (K_{wg} - 1) x^2 + x [(A + C) + (B - C)K_{wg}] - C = 0 \tag{4}$$

The procedure was modified slightly in the cases of Pittsburgh natural gas and ethane because these gases consisted of a mixture of hydrocarbons. In place of one mole of hydrocarbon a unit containing one mole of carbon was selected. The unit for Pittsburgh natural gas was therefore 1 mole of carbon, 1.85135 moles of hydrogen and 0.012965 mole of nitrogen: then $a = 1$, $b = 1.85135$, and the number of moles of nitrogen = $d + 0.012965$.

Choice of Data.—The heats of combustion of the hydrocarbons were calculated from data given in the "International Critical Tables."¹⁶ The heats given below are in calories per gram mole of hydrocarbon gas forming carbon dioxide gas and water vapor at 18° and a constant pressure of one atmosphere.

TABLE VI
HEATS OF COMBUSTION OF GASEOUS HYDROCARBONS

Formula	Name	Calories per gram mole
CH ₄	Methane	189,700
C ₂ H ₄	Ethylene	310,885
C ₂ H ₆	Ethane	336,732
C ₃ H ₆	Propylene	458,532
C ₃ H ₈	Propane	484,076
C ₄ H ₈	Butylene	604,976
C ₄ H ₁₀	Isobutane	630,620

H_{H_2O} at one atmosphere and 18° forming gaseous water = 57830 cal./mole,
 H_{CO_2} at one atmosphere and 18° = 67960 cal./mole.¹⁷

¹⁶ "International Critical Tables," Vol. V, 1929, pp. 138, 162.

¹⁷ "International Critical Tables," Vol. V, 1929, pp. 176, 181.

The free energy data for the water-gas reaction were taken from Eastman.¹⁸ The equilibrium constants at different temperatures were evaluated from the equation

$$\Delta F = 9800 - 3.06 T \ln T + 7.912 \times 10^{-3} T^2 - 2.358 \times 10^{-6} T^3 + 3.258 \times 10^{-10} T^4 + I_6 T$$

where $I_6 = 5.60$.

The equilibrium constants for the formation of water were calculated from the expression given by Lewis and Friauf¹⁹—valid up to 2800°K.

$$\log K_{p_{\text{H}_2\text{O}}} = \frac{57296}{4.573T} - 0.848 \log T - 1.474 \times 10^{-4} T + 7.78 \times 10^{-8} T^2 - 8.72 \times 10^{-12} T^3 + 0.616$$

The specific heat equations for the various gases are

$$C_{p_{\text{H}_2\text{O}}}^{20} = 8.32 - 6.53 \times 10^{-4} T + 2.70 \times 10^{-6} T^2 - 6.145 \times 10^{-10} T^3$$

$$C_{p_{\text{CO}_2}}^{21} = 7.70 + 5.30 \times 10^{-3} T - 0.83 \times 10^{-6} T^2$$

$$C_{p_{\text{H}_2}}^{19} = 6.64 + 4.92 \times 10^{-4} T + 0.319 \times 10^{-6} T^2 - 0.74 \times 10^{-10} T^3$$

$$C_{p_{\text{O}_2, \text{N}_2, \text{CO}}}^{19} = 6.73 + 4.08 \times 10^{-4} T + 0.486 \times 10^{-6} T^2 - 0.1234 \times 10^{-9} T^3$$

Method.—Given a certain initial mixture of hydrocarbon gas, air and water vapor: a value for T_2 is assumed and A , B and C are evaluated. These are substituted in (4), which is solved for x ; y is then obtained from (3). These values of x and y are substituted in the right-hand side of (1) and the value so found is compared with the true value of the equilibrium constant at the assumed temperature. If these do not agree, another temperature is assumed and the calculation repeated until they do agree. Both conditions of equilibrium and the energy equation are then satisfied. The amount of work may be materially lessened by constructing a plot of $\log K_{p_{\text{H}_2\text{O}}}$ vs. T . The values for the right-hand side of (1) (from two temperatures assumed on either side of the true temperature) are entered on the plot. The line of intersection is the true temperature, provided that the two assumed temperatures are not too far removed from each other.

The results of the calculations are plotted as dotted curves in Fig. 4, on a moisture-free and nitrogen-free basis and are comparable with the experimental curves. The maximum temperature for each combustible is listed in the last column of Table V.

Discussion

The character of the agreement between the calculated and observed flame temperatures is evident from an inspection of Fig. 4. Of most significance is the position of the maximum temperatures. These occur

¹⁸ E. D. Eastman, "The Free Energy of Water, Carbon Monoxide, and Carbon Dioxide," U. S. Bureau of Mines Information Circular 6125, 1929, p. 7.

¹⁹ Bernard Lewis and J. B. Friauf, *THIS JOURNAL*, 52, 3905 (1930).

²⁰ E. D. Eastman, unpublished report.

²¹ E. D. Eastman, "Specific Heats of Gases at High Temperatures." U. S. Bureau of Mines Technical Paper 445, 1929, p. 27.

for mixtures slightly on the rich side, as is the case for the observed temperatures. The difference between calculated and observed temperatures is about 100° for the unsaturated and about 40 to 70° for the saturated hydrocarbons. As is to be expected, this difference is greater, in general, the higher the temperature. It should be noted that the calculated and observed curves cross each other in the region of rich mixtures. This is probably due to the infiltration of secondary air which, burning some of the excess hydrocarbon, gives rise to observed temperatures higher than would have been recorded were secondary air absent.

If we assume that the specific heat and free energy data are reasonably correct, the difference is due to radiation losses from the flames.

It is of interest to record that a similar set of calculations assuming the gas to be dry give temperatures 42 to 50° higher than for wet gases.

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Summary

The flame temperatures for various hydrocarbon gas-air compositions have been measured for methane, Pittsburgh natural gas, ethane, propane, butane, isobutane, ethylene, propylene and butylene. The spectral-line reversal method was employed using sodium and lithium salt sprays. The flame temperatures reach a maximum when the mixture contains combustible slightly in excess of that necessary to consume all the oxygen present. These range from 1880° for methane to 1975° for ethylene. Comparison with the maximum speeds of uniform movement of flame shows that in general the latter is obtained for mixtures containing more combustible gas than those which give maximum flame temperatures. The flame temperatures of the various combustible gases have been calculated and the agreement is very satisfactory. The calculated maximum temperatures occur slightly on the rich side, as is the case for the observed values. These are higher than the observed values by about 100° for the unsaturated and 40 to 70° for the saturated hydrocarbons, and are in such a direction as to account for the difference by radiation losses from the flame.

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