

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

## THE FLAME TEMPERATURES OF MIXTURES OF METHANE-OXYGEN, METHANE-HYDROGEN AND METHANE-ACETYLENE WITH AIR<sup>1</sup>

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### Previous Investigations

The sodium line reversal method, first used by Kurlbaum,<sup>5</sup> has been used to determine the flame temperatures of mixtures of methane-oxygen, methane-hydrogen and methane-acetylene with air. This method has been described by Loomis and Perrott.<sup>6</sup> These investigators tried several known methods for measuring the temperatures of stationary flames, and finally adopted this method as being the most accurate and best adapted for the work.

Recently Jones, Lewis, Friauf and Perrott<sup>7</sup> reported results obtained on the flame temperatures of many hydrocarbon gases when mixed with air in varying proportions. They found that the flame temperature was markedly affected by the proportions of a given combustible hydrocarbon in air. The flame temperature increased rapidly, starting with a mixture near the lower limit of inflammability, and reached a maximum when the mixture contained combustible slightly in excess of that necessary to consume all the oxygen present. With further increases in percentage of combustible, the flame temperature decreased again, although not as sharply as for the mixtures containing excess oxygen.

The maximum flame temperatures of the gases tested varied from 1880° for methane to 1975° for ethylene, the maximum variation among the different hydrocarbons being less than 100°. The maximum flame temperatures of the unsaturated hydrocarbons were higher than those of the saturated hydrocarbons.

It was found that the composition of the combustible gas-air mixture which gave the highest flame temperature did not correspond to that for the highest speed of uniform movement of flame, except for methane and

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<sup>5</sup> Kurlbaum, *Physik. Z.*, 3, 332 (1902).

<sup>6</sup> A. G. Loomis and G. St. J. Perrott, *Ind. Eng. Chem.*, 20, 1004 (1928). See also Henning and Tingwald, *Z. Physik*, 48, 805 (1928), and Griffiths and Awbery, *Proc. Roy. Soc. (London)*, A123, 401 (1929).

<sup>7</sup> Jones, Lewis, Friauf and Perrott, *THIS JOURNAL*, 53, 869 (1931).

possibly Pittsburgh natural gas. For all the other hydrocarbon gases the mixtures which gave the highest flame temperatures contained less combustible gas than those which gave the highest speed of uniform movement of flame.

There was general agreement between the maximum flame temperature and maximum flame speed; the higher the temperature the higher the flame speed.

The calculated maximum flame temperatures were found to be about 100° higher than the observed for the unsaturated hydrocarbons and from 40 to 70° for the saturated hydrocarbons, the differences being accounted for by radiation losses. The calculated maximum flame temperatures were also slightly on the rich side.

**Flame Temperatures of Methane-Oxygen and Air Mixtures.**—The flame temperatures of methane-oxygen mixtures are of interest in view of the suggestion made by Little<sup>8</sup> that manufactured gas be freed of its poisonous constituent, carbon monoxide, thus making it safer for industrial and household uses. He proposed to convert the carbon monoxide and hydrogen by synthesis into methane and carbon dioxide and to remove the latter gas for utilization as a refrigerant. Manufactured gas would by this process consist largely of methane. The resulting non-poisonous gas consisting largely of methane was then to be mixed with oxygen in the proportion of about 80% of methane and 20% of oxygen. Little stated that the flame temperature of a gas of this composition burning in air would be about 10% higher than pure methane burning in air. Flame temperature determinations with methane-oxygen mixtures burning in air were therefore made to obtain information as to how rapidly the temperature increases with added oxygen.

The method used was the same as that described by Jones, Lewis, Friauf and Perrott,<sup>7</sup> to which reference should be made for details. Mixtures of approximately 90% of methane and 10% of oxygen, 85% of methane and 15% of oxygen, 80% of methane and 20% of oxygen and 77.5% of methane and 22.5% of oxygen were tested. The methane was obtained compressed in tanks to about 100 atmospheres of pressure from a well near Pittsburgh. Analysis of this gas at low temperatures and pressures, using a Shepard and Porter apparatus, gave the following results

Constituents.....	Methane	Ethane	Propane	Butane	Nitrogen
Per cent. by volume...	97.8	1.4	0.1	0.1	0.6

Compressed oxygen was used and analyzed better than 99.5% of oxygen. The required volumes of methane and oxygen were then metered into a 12-cubic foot water-sealed gas holder. The gases were thoroughly mixed, sampled and analyzed. The exact compositions of the different mixtures

<sup>8</sup> A. D. Little, *Am. Gas. Assoc. Monthly*, November, 1928, page 661.

are given in Fig. 1, in which are found the flame temperatures for varying air-gas ratios. It is seen that the maximum flame temperatures increase

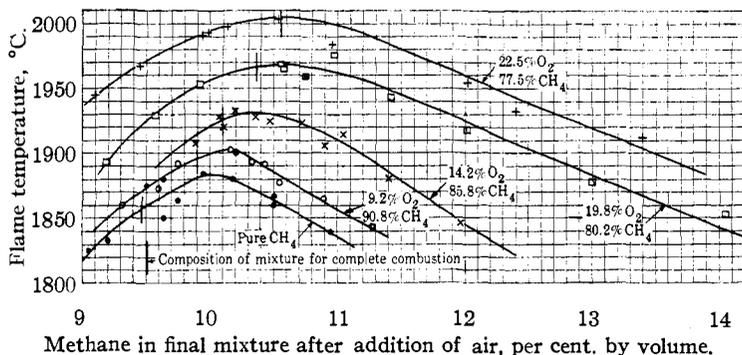


Fig. 1.—Flame temperatures of methane-oxygen-air mixtures.

with increasing amounts of oxygen; also the point at which the maximum temperature occurs shifts to the right with increasing oxygen con-

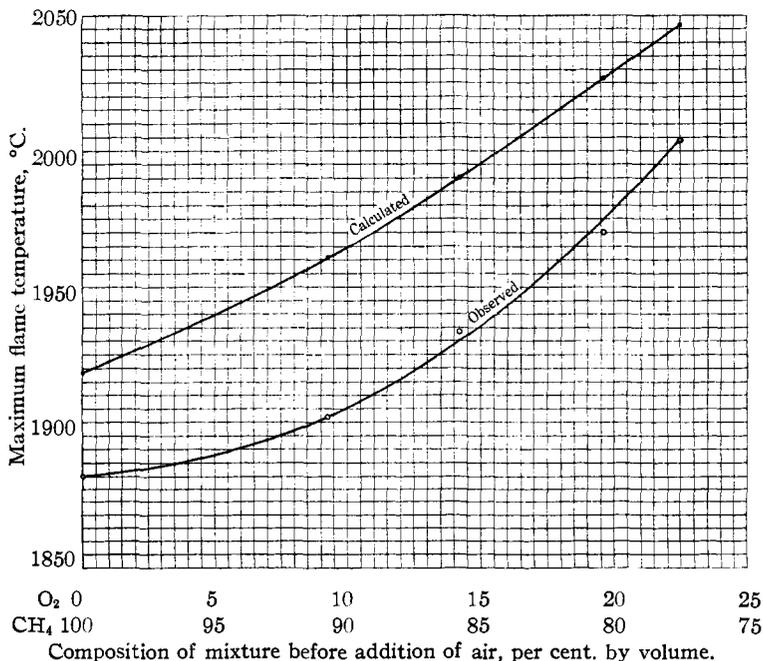


Fig. 2.—Maximum flame temperatures of methane-oxygen-air mixtures.

tent. The maximum flame temperatures for the different mixtures are shown better in Fig. 2. The maximum flame temperature of methane mixed with air is 1880° and of a mixture of 80% of methane and 20%

of oxygen 1974°. The percentage increase in flame temperature due to the presence of 20% of oxygen is approximately 5%, or about one-half that predicted by Little.<sup>8</sup> The calculated flame temperatures of these mixtures have been made following the method described by Jones, Lewis, Friauf and Perrott<sup>7</sup> and are given in Fig. 3. The variations between the maximum flame temperatures for the observed and calculated values are shown in Fig. 2. The calculated values are uniformly higher (about 40°) over the range tested. This difference is attributed to radiation losses. In both the calculated and observed curves the maximum temperature occurs somewhat on the rich side.

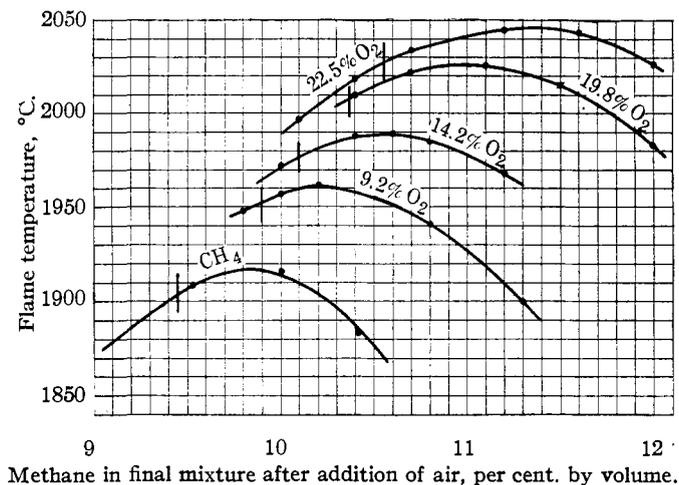


Fig. 3.—Calculated flame temperatures of methane-oxygen-air mixtures.

#### Flame Temperatures of Hydrogen-Methane and Air Mixtures.—

In certain industrial processes occasion may arise to raise or lower the temperature by admixture of another combustible gas. Therefore, various mixtures of hydrogen and methane were investigated, including pure methane and pure hydrogen to determine the manner in which the temperature increased as the mixture was made richer in hydrogen.

It was necessary to make a few changes in the design of the burner to prevent the mixtures of hydrogen and methane from flashing back through the burner. A Méker type burner (burner No. 3, Jones, Lewis, Friauf and Perrott)<sup>7</sup> with the addition of a 40-mesh nichrome screen both above and below the nickel grid was first used. Tests made with this burner caused the screens to heat up.<sup>9</sup> The nichrome screens were then removed

<sup>9</sup> Some interesting early results with the nichrome screens should be mentioned. Additions of hydrogen gave marked increases in flame temperature even when the burner was cooled by surrounding it with a moistened piece of felt. It was suspected that the

and copper screens used, and a circular copper disk having an opening so as to reduce the area of the burner one-half was inserted in the top of the burner. A sufficient velocity of the gas mixture passing through the burner could be obtained, so that the flame was prevented from "flashing back" into the burner, even when the mixtures contained as high as 80% of hydrogen and 20% of methane. For 100% of hydrogen the opening was reduced a little more. The methane used was the same as that in the methane-oxygen experiments. The hydrogen was obtained compressed in a steel cylinder and analyzed 99.5% of hydrogen with a small amount of oxygen and a trace of nitrogen.

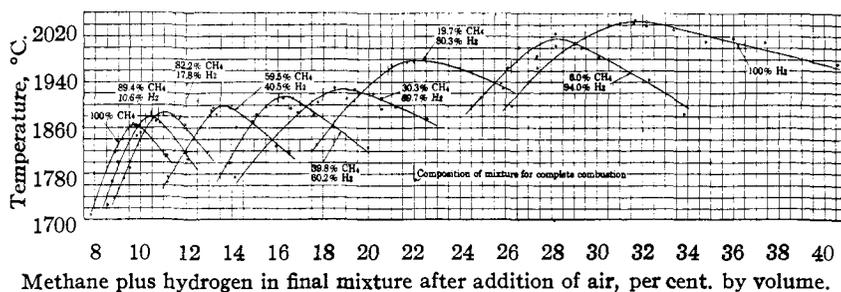


Fig. 4.—Flame temperatures of methane-hydrogen-air mixtures.

The mixtures were prepared in a manner similar to the methane-oxygen mixtures. The observed flame temperatures of the different methane-hydrogen mixtures mixed with varying amounts of air are given in Fig. 4. A set of calculated curves similar to Fig. 3 for methane-oxygen-air mixtures was made for methane-hydrogen-air mixtures, but it was thought unnecessary to include these. The observed and calculated maximum flame temperatures of the different methane-hydrogen mixtures are shown better in Fig. 5. As expected, the calculated temperatures are higher than the observed temperatures. Again the maximum temperatures lie somewhat on the rich side.

The maximum flame temperature of methane-air mixtures is 1875° (average value), while the maximum flame temperature for hydrogen-air mixtures is 2045°. The results bring out an interesting fact, namely, that the temperature is raised only a little by adding hydrogen to the extent of 50 to 60% to the original combustible mixture. Beyond 70% heating of the nichrome screen caused the increased temperatures because with this burner there was a thin zone in the flame just above the burner ports that was from 100 to 150° higher in temperature than the region above this zone. We have not succeeded in reproducing these results even with the conditions as nearly as possible the same, for the flame now appears uniform. It is not known whether the cause of the phenomena lay in some catalytic effect of solid particles from the nichrome screen, or whether it was due to some other source of an experimental nature.

hydrogen the temperature rises more rapidly. Indeed, with a 20% methane–80% hydrogen mixture the flame temperature comes to within some 85° of the flame temperature of 100% hydrogen. Obviously, therefore, there is little advantage in adding hydrogen to methane–air mixtures in small amounts to increase the flame temperature, but there is an advantage in adding methane to hydrogen–air mixtures in small amounts if a reduced flame temperature is desired in a reducing atmosphere.

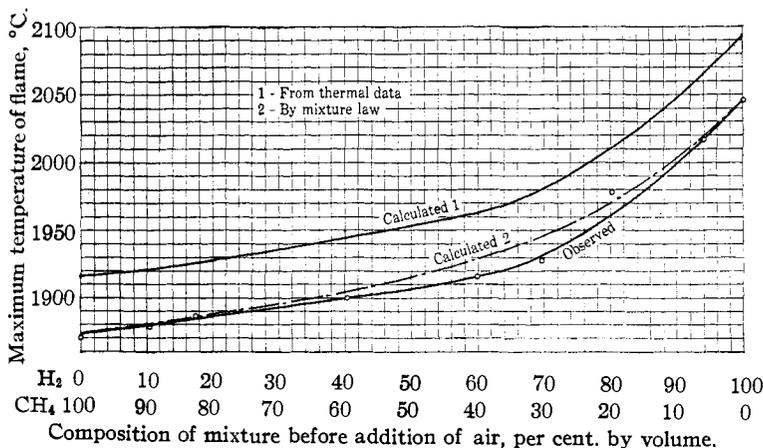


Fig. 5.—Maximum flame temperatures of methane–hydrogen–air mixtures.

#### Flame Temperatures of Methane–Acetylene and Air Mixtures.—

The flame temperature of various mixtures of methane and acetylene with air were determined, using the same procedure as that given for methane–hydrogen and air mixtures. It was necessary to purify the acetylene by passing the gas through a bath of carbon dioxide snow to remove acetone and other vapors before mixing with the methane in the gas holder.

The results obtained with the various mixtures are given in Fig. 6. There is a gradual and fairly uniform increase in the maximum temperature of the mixtures as the proportions of acetylene are increased. The percentage of combustibles in air (methane plus acetylene), at which the maximum flame temperature is found, decreases slightly as the proportions of acetylene are increased. The mixtures which contain just sufficient oxygen to consume all the combustibles are indicated on the graph by vertical lines. The mixtures which give the maximum flame temperatures are again slightly on the rich side to that necessary to give complete combustion.

The observed and calculated values of the maximum flame temperatures for the various mixtures tested are shown in Fig. 7. The values lie practically on a straight line. Temperatures were determined up to 20% of

methane, 80% of acetylene. Extrapolation of this line indicates that the maximum flame temperature for 100% acetylene is 2325°.

It is interesting that the slope of this temperature-composition curve is great enough to make it advantageous to add small amounts of acetylene to methane-air mixtures and obtain a considerable increase in flame temperature. Thus the addition of 20% of acetylene to the original combustible methane increases the temperature about 100°. Likewise, the temperature is lowered a similar amount by adding 20% of methane to the original combustible acetylene.

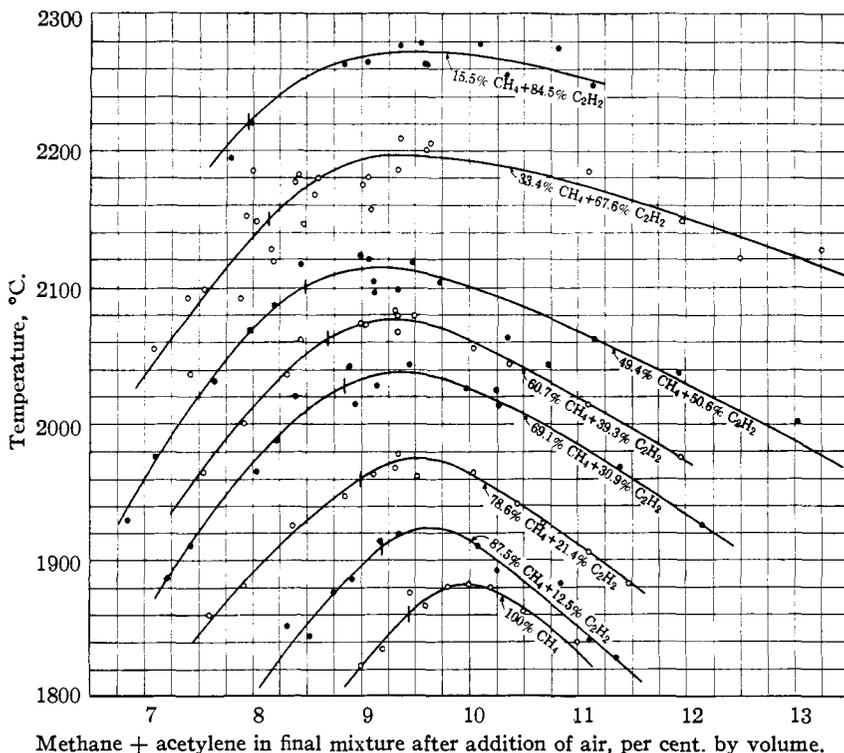


Fig. 6.—Flame temperatures of methane-acetylene-air mixtures.

**Application of the Mixture Law to the Calculation of Flame Temperatures.**—It is of interest to compare the observed maximum flame temperatures of the various mixtures of methane-hydrogen and methane-acetylene with those calculated by means of the well-known mixture law, which enables one to calculate the numerical value of any one property of a mixture of substances from the values of that property determined for the individual constituents of that mixture. Examples of the application of this law are the density of a mixture of gases which is de-

rived from the densities and relative volumes of the individual gases, and the limits of inflammability of complex gas mixtures which often can be quite accurately calculated if the composition of the mixture and the limits of inflammability of the individual combustible constituents are known.

This law, originally used by Le Chatelier,<sup>10</sup> was employed by Payman<sup>11</sup> to calculate the speed of uniform movement of flames. The two equations which Payman used may be applied to the calculation of maximum flame temperatures, by substituting temperature for speed. It is already known that a relationship exists between these two quantities.

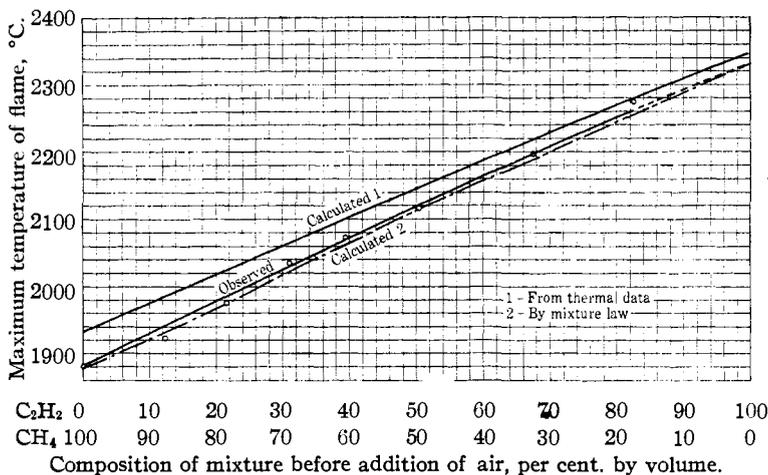


Fig. 7.—Maximum flame temperatures of methane-acetylene-air mixtures.

It is first necessary to determine the percentage of the mixed combustible gases in the maximum flame temperature mixture. For this purpose the following equation is employed

$$M = \frac{100}{\frac{P_1}{m_1} + \frac{P_2}{m_2} + \frac{P_3}{m_3} + \dots} \quad (1)$$

where  $M$  is the percentage of mixed combustible gases in the maximum flame temperature mixture,  $m_1, m_2, m_3, \dots$  are the percentages of the individual combustible gases in their own respective maximum flame temperature mixtures, and  $P_1, P_2, P_3, \dots$  are the percentages of the combustible constituents in the complex mixture on the air-free basis.

This value of  $M$  is now used to determine the values of  $a, b, c, \dots$  used in the equation

$$T = \frac{aT_a + bT_b + cT_c + \dots}{a + b + c + \dots} \quad (2)$$

<sup>10</sup> Le Chatelier, *Ann. des. Mines*, 19, 388 (1891).

<sup>11</sup> Payman, *J. Chem. Soc.*, 115, 1446 (1919).

where  $T$  is the maximum flame temperature required,  $a, b, c, \dots$  are the amounts of each combustible with air present in each maximum flame temperature mixture, and  $T_a, T_b, T_c, \dots$  are the maximum flame temperatures in each of these mixtures, respectively.

**Example.**—The experimental maximum flame temperature of hydrogen in air was found to be  $2045^\circ$  for a mixture containing 31.6% of hydrogen by volume in air. The experimental maximum flame temperature of methane in air was found to be  $1875^\circ$  (the average of many tests) for a mixture containing 9.9% of methane by volume in air. To calculate the maximum flame temperature of a mixture of methane and hydrogen containing, for example, 59.5% of methane and 40.5% of hydrogen,  $M$  is found from Equation 1.

$$M = \frac{100}{\frac{59.5}{9.9} + \frac{40.5}{31.6}} = 13.72\%$$

Then  $13.72 \times 0.595 = 8.16\%$  methane

$13.72 \times 0.405 = 5.56\%$  hydrogen

$$a = \frac{8.16}{9.9} = 0.824$$

$$b = \frac{5.56}{31.6} = 0.176$$

Substituting these values in Equation 2, one obtains

$$T = \frac{0.824 \times 1875 + 0.176 \times 2045}{0.595 + 0.405} = 1905^\circ$$

compared with an observed temperature for this mixture of  $1900^\circ$ .

The complete calculated curves for methane-hydrogen and methane-acetylene mixtures are given in Figs. 5 and 7, respectively. The agreement is remarkably good.

It would thus seem possible to calculate the maximum flame temperatures of complex mixtures from data on the individual constituents by the method outlined above. Experiments are in progress to test this for more complex mixtures than were used in this report.

### Conclusion

The flame temperatures of the binary mixtures methane-oxygen, methane-hydrogen and methane-acetylene with air at varying air-gas ratios are given. The observed values were determined by the sodium line reversal method described in previous reports.

The addition of oxygen to methane increases the maximum flame temperature when burned with air. When oxygen is added to methane until the mixture contains 20% of oxygen and 80% of methane, the maximum flame temperature of this mixture when burned with air is increased approximately 5%. The calculated values of maximum flame temperatures of the methane-oxygen mixtures are slightly higher than the ob-

served and the differences are approximately constant over the entire range tested.

The flame temperatures of methane-hydrogen mixtures in air were determined using mixtures varying from pure methane to pure hydrogen. As the hydrogen is increased, the maximum flame temperature increases only slightly up to about 80% of hydrogen, after which it increases rather rapidly. The calculated maximum flame temperatures of the mixtures tested are higher than the observed, and the differences are relatively the same over the entire range tested.

The flame temperatures of methane-acetylene mixtures with air were determined with various mixtures of the two above combustible gases from pure methane to 20% of methane-80% of acetylene. The maximum flame temperatures for the different mixtures lie practically on a straight line. The addition of small amounts of acetylene to pure methane causes a considerable increase in the flame temperature. It was impossible to determine the flame temperature of pure acetylene in air, but a small extrapolation indicates a maximum flame temperature of this mixture of 2325°. The calculated maximum flame temperatures are higher than the observed and the differences decrease at the higher flame temperatures.

The maximum flame temperatures of all the binary mixtures tested show that the highest temperature is reached when the mixtures are slightly on the rich side—that is, those having an insufficient amount of oxygen present to consume all the combustible present. This is in agreement with previous tests made with single hydrocarbon gases with air.<sup>7</sup>

The calculated flame temperatures for the binary hydrocarbon gases with air are slightly higher and in good agreement with the observed values, considering radiation losses. The results given here and elsewhere<sup>7</sup> indicate that the flame temperatures of hydrocarbons or mixtures of hydrocarbons with air may be calculated almost as accurately as direct observations, using the sodium line reversal method.

The mixture law is applied to mixtures of combustible gases and it is shown that the maximum flame temperature of any mixture of methane-hydrogen and methane-acetylene can be calculated from a knowledge of the maximum flame temperatures of the individual combustible mixtures.

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