## Summary

1. The dissociation of gaseous ethyl bromide into ethylene and hydrobromic acid has been determined between 395 and 420° and at pressures ranging from 12 mm. to 360 mm. It is a unimolecular reaction suitable for the study of kinetics.

2. Ethyl bromide was sealed off in glass vessels totally immersed in a lead thermostat controlled by a photoelectric cell. The pressure was followed through a glass diaphragm.

3. The influence of traces of air was studied.

4. The unimolecular dissociation is accompanied by a bimolecular recombination. Four different methods for calculating the specific decomposition rate $k$ are discussed.

5. The specific rate $k$ starts to decrease at pressures below 100 mm. and at lower pressures the reaction tends to follow the second order equation.

6. The data above 100 mm. pressure are well expressed by the formula, $k = 3.85 \times 10^{14} e^{-54,800/RT}$.

7. The data are used to test collision theories of unimolecular reactions. They do not agree well with the predictions of Theory I. The temperature coefficients at high and low pressures suggest a better agreement with Theory III or II.

8. A relay switch is described which operates only on alternate excitations.

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

# The Effect of an Electric Field on the Flame Temperature of Combustible Gas Mixtures[1]

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The effect of an electric field on the flames of a number of combustible gases has been reported on by several investigators.[4] It was found that the electric field exerted a marked influence, increasing or decreasing the speed of propagation of the flame (depending on experimental conditions), seriously deforming and weakening the appearance of the flame, and under suitable conditions eventually extinguishing it completely.

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Mines, the Carnegie Institute of Technology, and the Mining Advisory Board, the present work was undertaken to determine what effect, if any, the electric field had on the flame temperature. In all cases investigated a lowering of the flame temperature was observed to a more or less degree, which depended on the composition of the gas mixture and certain mechanical details described below.

## Method and Procedure

The sodium line reversal method was used for determining flame temperatures. The same apparatus was employed as in previous investigations.[5] The method of applying a high direct potential was the same as reported previously.[4]

The burner consisted of 32 porcelain tubes (*ca.* 3-mm. bore) closely packed together and cemented gas-tight into the opening of a small brass box 5.5 by 3.5 cm. similar to those described in Fig. 2 of the paper by Jones, Lewis, Friauf and Perrott.[5] To meet the requirements of faster or slower burning mixtures, tubes of smaller or larger bore could be substituted. The electrodes consisted of two brass plates 6 cm. square containing a hole 8 mm. in diameter, two-thirds the distance up, through which the light beam, essential in the line reversal method, passed. The electrodes were mounted on porcelain rods which were attached to the brass box and which were movable up or down with respect to the burner tips. Observations could therefore be made at different heights of the flame, exposing more or less of the latter to the action of the field. The electric field was applied across the flame—*i. e.*, in the direction of the light beam. Thus, if the flame was distorted by the field it was not displaced from the axis of the light beam. To prevent the flame from touching the negative electrode toward which it was pulled when the field was applied, this electrode was placed 1.5 cm. farther from the center of the group of burner tips than the positive electrode. In this way cooling by contact with the electrode was eliminated. The over-all distance between the electrodes was 6 cm., while the diameter across the burner tips was 2.5 cm. Care was taken to ensure that the flame did not touch the electrode below the point of observation. Above the point of observation the flame sometimes approached the electrode sufficiently close to allow thin sparks to pass between it and the flame boundary. Readings were not taken under these conditions, but the potential was lowered to avoid this. Temperature readings with the electric field were sandwiched between readings without the field. The potential could be varied up to about 18,000 volts.

The combustible gases used were Pittsburgh natural gas, ethylene, isobutane and butylene mixed with air. Three mixtures were used for each gas, one giving approximately a maximum flame temperature (close to theoretical oxygen content), and the others rich and lean mixtures. For the first mixture, readings were made at intervals of 1 cm. from 0.5 cm. to 6.5 cm. above the burner tips. For the rich and lean mixtures observations were made only at 6.5 cm. Gas samples were collected and analyzed on a Bone–Wheeler apparatus.

Finally some observations were made of the effect of an electric field on a very low-temperature and a high-temperature flame of carbon disulfide vapor.

## Results

A summary of the results is given in Table I and illustrated in Fig. 1. The curves in the figure are for the approximately maximum temperature mixtures. An effect of less than 9° is ignored.

(5) Loomis and Perrott, *Ind. Eng. Chem.*, **20**, 1004 (1928); Jones, Lewis, Friauf and Perrott, THIS JOURNAL, **53**, 869 (1931); Jones, Lewis and Seaman, *ibid.*, **53**, 3992 (1931); **54**, 2166 (1932).

TABLE I

SUMMARY OF RESULTS OF EFFECT OF ELECTRIC FIELD ON FLAME TEMPERATURES

| Height above burner, cm. | Flame temperatures: Natural gas, Per cent. of gas | No field, °C. | With field, °C. | $\Delta T$ | Ethylene, Per cent. of gas | No field, °C. | With field, °C. | $\Delta T$ | Isobutane, Per cent. of gas | No field, °C. | With field, °C. | $\Delta T$ | Butylene, Per cent. of gas | No field, °C. | With field, °C. | $\Delta T$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.5 | 9.06 | 1775 | 1772 | .. | 6.95 | 1923 | 1916 | ... | 3.59 | 1802 | 1802 | .. | 3.93 | 1844 | 1842 | .. |
| 1.5 | 9.06 | 1851 | 1848 | .. | 6.95 | 1966 | 1942 | 24 | 3.59 | 1851 | 1841 | 10 | 3.93 | 1864 | 1862 | .. |
| 2.5 | 9.06 | 1835 | 1828 | .. | 6.95 | 1966 | 1950 | 16 | 3.59 | 1848 | 1838 | 10 | 3.93 | 1848 | 1842 | .. |
| 3.5 | 9.06 | 1809 | 1794 | 15 | 6.95 | 1933 | 1924 | 9 | 3.59 | 1844 | 1828 | 16 | 3.93 | 1848 | 1848 | .. |
| 4.5 | 9.06 | 1770 | 1752 | 18 | 6.95 | 1912 | 1892 | 20 | 3.59 | 1821 | 1812 | 9 | 3.93 | 1843 | 1832 | 11 |
| 5.5 | 9.06 | 1756 | 1725 | 31 | 6.95 | 1919 | 1900 | 19 | 3.59 | 1802 | 1764 | 38 | 3.93 | 1832 | 1806 | 26 |
| 6.5 | 9.06 | 1737 | 1686 | 51 | 6.95 | 1868 | 1780 | 88 | 3.59 | 1782 | 1743 | 39 | 3.93 | 1811 | 1776 | 35 |
| 6.5 | 7.15 (lean) | 1649 | 1597 | 52 | 4.67 (lean) | 1595 | 1479 | 116 | 1.85 (lean) | 1712 | 1647 | 65 | 3.82 (lean) | 1811 | 1760 | 51 |
| 6.5 | 10.0 (rich) | 1739 | 1718 | 21 | 10.98 (rich) | 1830 | 1818 | 12 | 3.92 (rich) | 1733 | 1710 | 23 | 5.0 (rich) | 1742 | 1735 | .. |

It is observed that the lowering of the flame temperature increases as more of the flame is exposed to the field below the point of observation. One would expect, therefore, that the effect would be lessened if the gases were exposed to the field for a shorter time. This was found to be the case when an ethylene mixture was passed through the burner with a greater velocity. A mixture deficient in oxygen was not used for butylene.

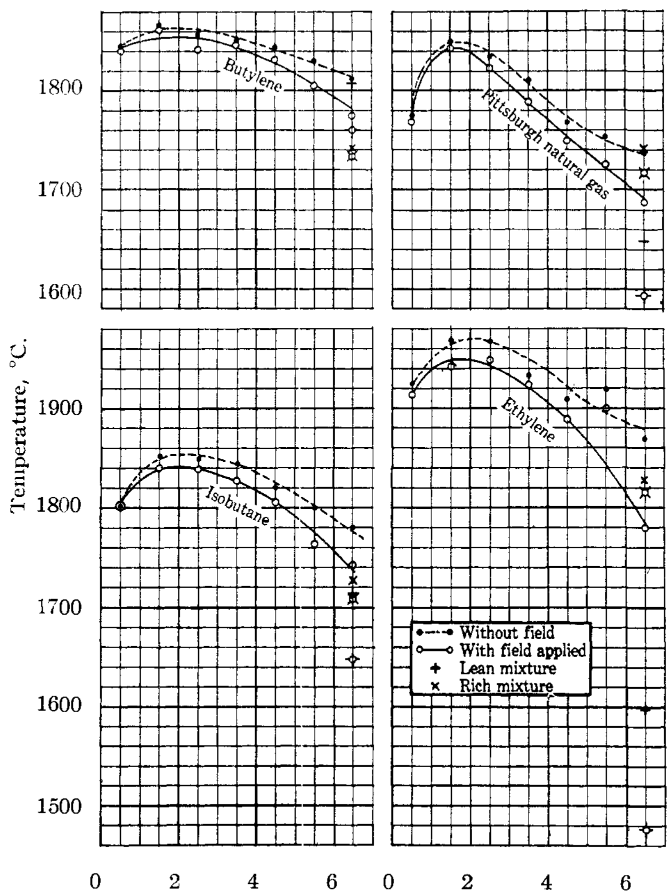


Fig. 1 —Effect of electric field on flame temperatures.

There is a remarkable difference between the effects on rich and lean mixtures. In all cases the effect is small for rich mixtures but large for lean mixtures. Thus, for example, the temperature lowering for ethylene is 12° for a rich and 116° for a lean mixture.

The authors wish to present the experimental facts but are not disposed to discuss the meaning of the results at the present stage of progress.

It was of interest to see whether a low-temperature flame could in any way be affected or distorted by the electric field. A stream of carbon disulfide vapor was passed through the burner. The air necessary for combustion was picked up after leaving the burner tips. The resulting flame had a temperature of the order of 100°. The amount of ionization in such a flame is negligible. The flame was unaffected by a high electric field. However, a high-temperature flame of carbon disulfide (about 1600–1700°), produced by premixing the air in which there is probably a considerable amount of ionization, was affected as other high-temperature flames are. Readings of the temperature-lowering effect of the field in the latter flame were unreliable due to inconstancy of the mixture under the present arrangement.

## Summary

The effect of an electric field applied transversely across a flame, on the flame temperatures of rich, lean and nearly theoretical mixtures of Pittsburgh natural gas, ethylene, isobutane and butylene in air was investigated using the sodium line reversal method for measuring their flame temperatures. In all cases investigated the effect of the field was to reduce the flame temperature. This was greatest the slower the gas velocity and the greater the length of flame which was exposed to the field before observations were made. The greatest effect was found for lean mixtures and the smallest for rich mixtures. Thus, for ethylene the temperature lowering for a lean mixture was 116° and for a rich mixture 12°.

It was shown that a low-temperature flame of carbon disulfide vapor is unaffected by an electric field but that a high-temperature flame of the same combustible vapor is deflected toward the negative electrode as are the flames of other combustibles.

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