Summary

1. A new twin-ring tensiometer enabling the error of relative surface tension measurements to be reduced to 0.002% is described.

2. Surface tension measurements of potassium chloride solutions at 25° have been made over a wide concentration range. Agreement with similar data of Jones and Ray is so close that no consideration need be made of the Harkins F-factor.

3. The data confirm the Jones–Ray effect; the minimum of the surface tension occurs at 0.001 N potassium chloride solution as in Jones and Ray's work, but we find the apparent lowering of the surface tension to be 0.03% instead of 0.02%.

4. We have not been able to demonstrate any applicability of the Langmuir film theory to our data, and conclude, therefore, that the validity of the Langmuir theory as an explanation of the Jones–Ray effect, is questionable.

Combustion of Methane: Displacements of Mixtures Giving Maximum Flame Velocities[1]

BY A. R. T. DENUES[2] WITH WILBERT J. HUFF

I. Introduction

In the slow propagation of flame in gases it has long been recognized and generally accepted that mixtures giving maximum flame velocities[3] are displaced toward excess combustible from the stoichiometric mixtures for complete combustion.[4,5] These displacements[6] are a fundamental characteristic that must be accounted for by any adequate theory of the mechanism of flame propagation. In practical applications where the maximum thermal or mechanical output must be secured from minimum gas volumes, or where variations in thermal output may be critical, an understanding of the magnitude of this displacement and its variation with changes in mixture composition may be important.

Despite the long and general recognition of displacements, some recent writers have apparently doubted their existence for methane and for natural gas consisting principally of methane[7];

this called attention to the phenomenon for this gas. Computations based upon published data for carbon monoxide and hydrogen[8] give regular relationships between the displacements and the content of oxygen in the atmosphere. In contrast, the analogous relation for methane was not established by available data.

Thus, it was noted from Jahn's data,[8] which are perhaps the most complete measurements, made by the burner method, of flame velocities pertinent to this discussion, that curves relating the displacements and the oxygen content of the atmosphere used for the combustion of hydrogen and of carbon monoxide could be derived that appeared continuous and exhibited maxima, but that a similar relation for methane was quite uncertain. The positions of the maxima of flame velocity reported by Jahn for methane, excluding apparently extrapolated values, lead to displacements of 0.9, 1.1, 1.2, 1.3, 1.2, 0.9 and 0.0 in order as the oxygen content of the atmosphere increases in the series 21, 25, 30, 40, 60, 80, and 98.5 volume-per cent. Except for the value for combustion with substantially pure oxygen, these displacements average 1.1 with an average deviation of about 0.1. In view of the lack of precision measures in Jahn's paper and the magnitude of the precision measures recorded for similar work in a later section of the present discussion, it must be concluded from Jahn's data that the displacements for methane in atmospheres other than pure oxygen are substantially independent of the oxy-

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(3) "Flame velocity" as used here denotes the rate of movement of flame during the slow, uniform period, relative to the unburned gas and in a direction normal to the flame surface.

(4) E. Mallard, *Ann. Mines*, [7] **7**, 355 (1875).

(5) W. Michelson, *Ann. Phys. Chem.*, [3] **37**, 1 (1889).

(6) This divergence of mixture giving maximum flame velocities from the stoichiometric mixtures for complete combustion will be abbreviated in this paper to the term "displacement."

(7) Thus: Haslam and Russell, "Fuels and their Combustion," McGraw-Hill Book Co., Inc., New York, N. Y., 1926, p. 268, state that the maximum speed occurs when the methane and oxygen are in combining proportions, and "Combustion," American Gas Association, New York, N. Y., 1932, p. 92, gives a curve of flame speed *vs.* primary air–gas ratio that indicates that the maximum speed natural-gas–air mixture is displaced toward excess air.

(8) G. Jahn, "Der Zündvorgang in Gasgemischen," R. Oldenbourg, Berlin, 1934.

gen content. This conclusion stands in contrast to the unequivocally regular relations exhibiting maxima that are cognizable from Jahn's data for the combustion of hydrogen and of carbon monoxide.[9]

Collectively, these circumstances indicated a need for the investigation mentioned to determine whether or not a continuous relation exists between the displacements and the oxygen content of the atmosphere used for combustion of methane, analogous to the relations derived from data published for other gases, and if it exists, whether or not this relation possesses a maximum analogous to that exhibited by other gases.

II. Materials, Apparatus and Method

As qualitative results seemed sufficient for the purposes given, measurements of an essentially relative character were deemed adequate. A large cylinder of a commercial
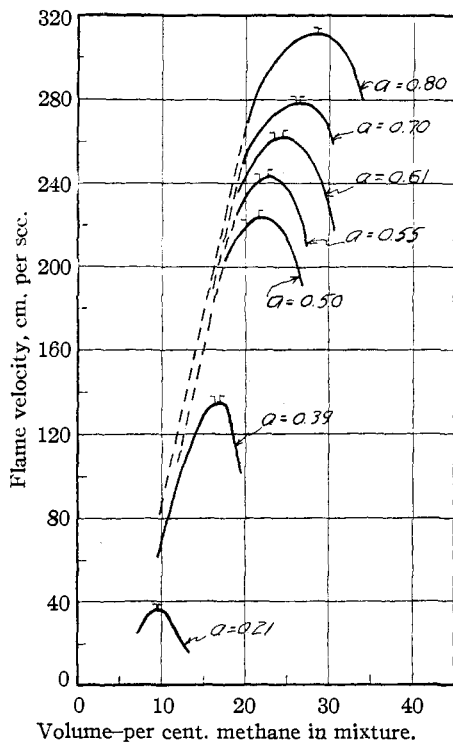

Fig. 1.—Relations between flame velocity for methane and content of methane in mixture for combustion with various atmospheres. (a represents volume fraction of oxygen in atmosphere.)

(9) In addition, it may be interesting to note that even though data obtained by the tube method are of limited value for comparisons with data obtained by the burner method, such a comparison was made here because of the paucity of data. This, however, only confused the situation because studies of methane burned with atmospheres embracing the entire range of feasible oxygen contents [W. Mason, and R. V. Wheeler, J. Chem. Soc., 111, 1044 (1917); Payman, William, ibid., 117, 48 (1920)] showed marked irregularities in the relations in question.

methane containing so small a proportion of ethane as to have no effect on the trends obtained was used; analysis by a Bureau of Mines Orsat indicated methane 96.7 vol. %, air 3.3 vol. %. The commercial compressed oxygen and nitrogen employed contained 99.5 ± 0.1% of their major constituents.

Flame velocities were determined in duplicate by the burner method using an apparatus essentially similar to that described by Smith and Pickering.[10] The studies included combustion with atmospheres containing nitrogen and between 20 and 80 volume-per cent. oxygen. The gases were preheated to 40 ± 0.1°. The height of the inner cone of the Bunsen flames obtained, measured by cathetometer, was used in calculating the flame velocities; this procedure introduced no significant errors because the measurements were confined to mixtures that differed only slightly from those giving maximum flame velocities.

Maximum determinate relative errors of 1% in the fraction of methane in the mixtures and in the flame velocities were deduced. This figure is a fair precision measure for the first quantity, but the precision measure for the flame velocities should be given as within 2%.

III. Experimental Results

Summarized data are represented in Fig. 1 as a system of relations between the flame velocity and the content of methane in mixture with a given atmosphere, the oxygen content of this atmosphere being treated as a variable parameter. Coördinates of the maxima of these curves, derived from suitable large-scale graphs with the aid of the differentiated form of Newton's formula for interpolation, are summarized below together with the displacements.

TABLE I
SUMMARIZED RESULTS

Volume-fraction O_2 in atmosphere	Max. flame velocity, cm./sec.	Stoichiometric mixture	Volume-fraction CH_4 in Mixture for max. flame velocity	Displacement Actual	%[b]
0.209	36.4	0.095	0.097	0.002	2.1
.390	137	.163	.170	.007	4.3
.500	216	.200	.215	.015	7.5
.552	243	.216	.227[a]	.011[a]	5.1
.607	262	.233	.243	.010	4.3
.651	265	.246	.254[a]	.008[a]	3.3
.701	278	.260	.265	.005	1.9
.800	307	.286	.287	.001	0.4

[a] Approximate. [b] Per cent. of stoichiometric mixture.

The relations between the displacements and the fraction of oxygen in the atmosphere used for combustion plotted in Fig. 2 appear continuous and exhibit maxima.

IV. Discussion

Flame Velocities.—The flame velocities obtained for combustion with air agree well with

(10) F. A. Smith and S. F. Pickering, U. S. Bur. Standards Research Paper 900 (1936).

the results of previous measurements by similar methods. Divergences of variable magnitude that average about 15% exist between the remainder of the present results and the only data[8] available for further comparisons; these divergences appear explicable. An extrapolated maximum flame velocity of 320 cm. per sec. for the combustion of methane with pure oxygen is in fair agreement with the value 333 reported by Jahn[8]; this supports the previously unverified divergence between Jahn's value and the values obtained by Ubbelohde and Dommer[11] and by Stevens.[12]

Displacements.—In common with previous measurements by various methods, the present results show relatively small displacements for methane. However, the relations established between these displacements and the concentration of oxygen in the atmosphere used for combustion stand in marked contrast with previous results for methane as reviewed in the introduction to this paper, and complement analogous relations derived by the writers from data published for the combustion of hydrogen and of carbon monoxide. The continuous relation, showing a maximum, between the displacement and the oxygen content of the atmosphere used for combustion seems therefore to be a common characteristic for both types of ordinary combustible gases.

(11) L. Ubbelohde and O. Dommer, *J. Gasbeleucht.*, **57**, 757 (1914).
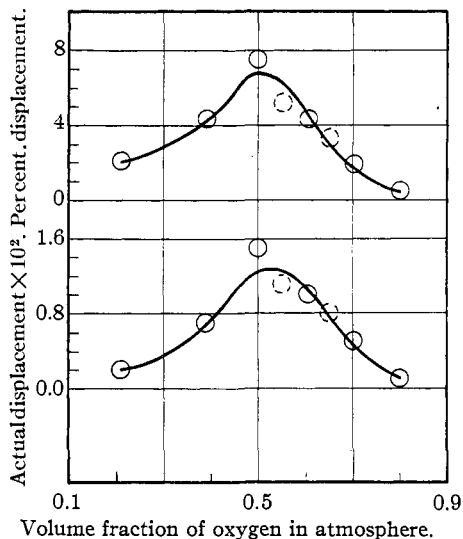(12) F. W. Stevens, *Natl. Advisory Comm. Aeron. Repts.*, 305 (1929).

Fig. 2.—Relations between displacements of mixtures giving maximum flame velocities for methane and the composition of the atmosphere used for combustion.

V. Summary

Data showing effects of the oxygen content of atmospheres used for the combustion of methane on flame velocities and on displacements of mixtures giving maximum flame velocities are presented and discussed briefly. A new regularity between these displacements in the combustion of methane and the parameter cited has been adduced that contrasts with earlier indications for methane and complements relations derived by the writers from published data for other gases.


[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

Acid–Base Equilibria in Methyl Alcohol[1]

BY MARTIN KILPATRICK AND WHITNEY H. MEARS

In a previous paper[2] it was shown that equilibrium constants between acids and bases could be determined by the colorimetric method, and the thermodynamic constants obtained by extrapolation. The present paper deals with the effect of ionic strength on the equilibrium

$$A_i^- + B^- = A^0 + B_i^-$$
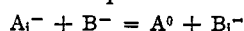
in the solvent methyl alcohol. A_i^- represents the yellow form of brom phenol blue or brom cresol

(1) Aided by a grant from the Penrose Fund of the American Philosophical Society.
(2) Minnick and Kilpatrick, *J. Phys. Chem.*, **43**, 259 (1939).

green, B^- represents benzoate ion or its monosubstituted derivative, A^0 represents the conjugate acid and B_i^- the blue form of the indicator. Two methods of extrapolation to infinite dilution are considered and acid strengths relative to benzoic acid calculated from the data.

Experimental Part

Preparation of Compounds.—Commercial anhydrous methyl alcohol was purified by the method of Lund and Bjerrum.[3] A three-hour refluxing with anhydrous copper

(3) Lund and Bjerrum, *Ber.*, **64B**, 210 (1931).