

Burning velocities of 7, 8 and 9 per cent ethylene/air mixtures in cm./sec. The values for pressures of 17 cm. of mercury are in brackets as their degree of accuracy is considerably less than the rest of the values.

Pressure (cm. of Hg)	7%	8%	9%
77	71	71	59
70	72	72	61
64.5	70	72	65
56	76	77	66
49	81	81	70
37	89	91	81
27	97	98	87
(17)	(109)	(108)	(103)

by Linnett and Sherratt¹⁰. The results for 7, 8 and 9 per cent mixtures are given in the accompanying table. Although the absolute values of the burning velocities given here may be as much as 5 per cent in error, their relative values are much more accurate, and the figures show that the burning velocity increases steadily as the pressure is reduced. Moreover, they are in quite good agreement with Tanford and Pease's prediction¹¹ that the burning velocity should vary inversely as the fourth root of the pressure. Although the agreement with their purely diffusion theory is so good, we do not believe that diffusion alone can account for all the intricacies of flame propagation, and it is significant that a purely thermal theory also leads to the expectation that the burning velocity should increase as the pressure decreases¹².

We are at present constructing an apparatus with which we hope to investigate more fully the effect of pressure on the burning velocity of explosive gas mixtures. However, an examination of the literature, together with our own limited experience, had led us to believe that most of the present evidence indicates that burning velocities are affected by pressure and that, for some hydrocarbons, as the pressure is lowered the burning velocity increases.

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¹ Gaydon and Wolfhard, *Proc. Roy. Soc., A*, **196**, 105 (1949).

² Wolfhard, *Z. tech. Phys.*, **24**, 206 (1943); results using acetylene as the combustible gas.

³ Ubbelohde and Koelliker, *J. Gasbel.*, **59**, 49 (1916).

⁴ Khitrin, *Tech. Phys. U.S.S.R.*, **3**, 926 (1936).

⁵ Kolodtsev and Khitrin, *Tech. Phys. U.S.S.R.*, **3**, 1034 (1936).

⁶ Ubbelohde and Andwandter, *J. Gasbel.*, **60**, 225 (1917).

⁷ Stevens, Nat. Advisory Comm. Aeronaut. Reports, 372 (1931).

⁸ Flock and Roeder, Nat. Advisory Comm. Aeronaut. Reports, 532 (1935).

⁹ Garside, Forsyth and Townend, *J. Inst. Fuel*, **18**, 175 (1945).

¹⁰ Linnett and Sherratt, *Trans. Farad. Soc.*, **44**, 596 (1948).

¹¹ Tanford and Pease, *J. Chem. Phys.*, **15**, 861 (1947).

¹² Jouguet, *C.R. Acad. Sci., Paris*, **168**, 820 (1919); **179**, 454 (1924). Daniell, *Proc. Roy. Soc., A*, **126**, 393 (1930).

To determine the true dependence of flame velocity on pressure it is necessary to make a large number of measurements, because the velocity is not exactly constant within the stability region (see Wolfhard¹). To make comparable measurements it is especially necessary to increase the burner diameter as the pressure is reduced, so that the diameter is inversely proportional to pressure. This was done for our measurements, but not for the older results referred to by Linnett and Wheatley. We do not deny that for the acetylene/air flame the flame velocity tends to increase slightly as the pressure is reduced; but at still lower pressure the velocity

decreases again, and the effect is probably due to the nitrogen. For flames in which the nitrogen of the air is replaced by argon, we have not observed any measurable change of velocity with pressure. We would emphasize that our results, especially for oxy-acetylene flames, are based on a very large number of measurements with various burner diameters and cover a big range of pressure (from 1 atm. to less than 0.01 atm.).

The main purpose of our paper was to point out the relationship between the thickness of the luminous reaction zone and the distance which free atoms may diffuse against the gas stream. Our calculations of the dependence of velocity on pressure are only approximate, but appear to be a better approximation than the treatment of Tanford and Pease, which leads to the inverse fourth root law for the variation of velocity with pressure.

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¹ Wolfhard, H. G., *Z. tech. Phys.*, **9**, 206 (1943).

Photochemical Polymerization in Aqueous Solution

A NEW series of polymerization photo-sensitizers in aqueous solution, which is based on electron transfer excitation, is described for the first time. E. Rabinowitch¹ has interpreted the absorption spectra of some ion pairs such as $\text{Fe}^{3+}\text{OH}^-$, $\text{Fe}^{3+}\text{Cl}^-$, etc., as electron transfer spectra. The light absorption would, according to his hypothesis, cause the reduction of the metal ion and the oxidation of the anion to an atom or free radical; thus, for example, $\text{Fe}^{3+}\text{OH}^- \rightarrow \text{Fe}^{2+}\text{OH}$. No experimental evidence has been forthcoming which would demonstrate the presence of the latter in the irradiated solution. In this note we present such evidence, and this is based on the ability of these photochemically produced radicals or atoms to initiate the polymerization of vinyl compounds under conditions ($h\nu > 300 \text{ m}\mu$) in which no direct photopolymerization of the corresponding monomers would occur.

The general scheme may be illustrated with reference to $\text{Fe}^{3+}\text{OH}^-$:

- $\text{Fe}^{3+}\text{OH}^- \rightleftharpoons \text{Fe}^{2+}\text{OH}$ Excitation and primary dark back reaction.
- $\text{Fe}^{2+}\text{OH} \rightarrow \text{Fe}^{2+} + \text{OH}$ Separation of primary products.
- $\text{Fe}^{2+} + \text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^-$ Secondary dark back reaction.
- $\text{Fe}^{2+}\text{OH} + M \rightarrow \text{HO}-M- + \text{Fe}^{2+}$
 $\text{OH} + M \rightarrow \text{HO}-M-$ } Initiation of polymerization. (M represents a vinyl monomer)
- Possible recombination of OH radicals and subsequent reactions

Baxendale, Evans *et al.*² have shown that OH radicals produced in the ferrous iron-hydrogen peroxide reaction may initiate polymerization in such compounds as acrylonitrile, methyl methacrylate, styrene, etc.

The same monomers were found to polymerize when solutions of $\text{Fe}^{3+}\text{OH}^-$ and monomer were irradiated with ultra-violet light of wave-length $> 300 \text{ m}\mu$. Monochromatic light of wave-length as high as $365 \text{ m}\mu$ was also found to lie within the effective range of wave-lengths. In the presence of monomers the rate of ferrous ion formation leads to quantum yields up to $\sim 10^{-2}$ (for $365 \text{ m}\mu$) with saturated solutions ($1.2 M$) of acrylonitrile. It is because of the low