AIP | The Journal of Chemical Physics

Composition Profiles in PreMixed Laminar Flames

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Citation: The Journal of Chemical Physics **22**, 145 (1954); doi: 10.1063/1.1739826
View online: http://dx.doi.org/10.1063/1.1739826
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/22/1?ver=pdfcov
Published by the AIP Publishing

$$(v_L(I_a)+v_R(II))y^{C_2H_4(a)}=v_R(I_a)y^{C_2H_4}$$
$$+v_L(II)(y^{C_2H_5(a,0)}+\tfrac{1}{3}y^{C_2H_4D(a,1)}), \quad (4)$$
$$(v_L(II)+v_R(III))y^{C_2H_5(a,0)}=v_R(II)y^{C_2H_4(a)}y^{H(a)}$$
$$+v_L(III)(y^{C_2H_6}+\tfrac{1}{6}y^{C_2H_5D}).$$

……

Putting $y^{C_2H_4}=y^{D_2}=1$ in the foregoing equations and eliminating $y^{\delta(a)}$'s among them, we have $\dot{Y}^{H_2}$, etc., at the initial stage of the reaction. From those results,

$$\dot{Y}^{H_2}:\dot{Y}^{HD}=1:2\Omega, \quad \Omega=y^{D(a)}/y^{H(a)} \quad (5)$$

is derived exactly and the following are obtained with use of conclusion (C):

$$\dot{Y}^{C_2H_3D}:\dot{Y}^{C_2H_2D_2}:\dot{Y}^{C_2HD_3}:\dot{Y}^{C_2D_4}=1:R/2:R^2/6:R^3/36, \quad (6)$$
$$\dot{Y}^{C_2H_6}:\dot{Y}^{C_2H_5D}:\dot{Y}^{C_2H_4D_2}:\dot{Y}^{C_2H_3D_3}:\dot{Y}^{C_2H_2D_4}:\dot{Y}^{C_2HD_5}:\dot{Y}^{C_2D_6}$$
$$=1:2\Omega:\Omega^2:2R\Omega^2/3:R^2\Omega^2/3:R^3\Omega^2/9:R^4\Omega^2/54, \quad (7)$$

where

$$R=y^{D(a)}v_L(II)/v_L(I_a)\ll 1 \quad (8)$$

and

$$\Omega=v_R(I_b)/(v_L(I_b)-v_R(I_b))+\tfrac{1}{3}v_L(II). \quad (9)$$

Applying this to the experimental condition of Turkevich *et al.* (below the optimum temperature), we have from conclusion (B)(i),

$$\Omega=3v_R(I_b)/v_L(II)\ll 1. \quad (10)$$

It follows from (8) and (10) that relations (6) and (7) both decrease regularly with increasing substitution of deuterium, just as observed by Turkevich *et al.*

We might now add a few theoretical predictions. Above the optimum temperature, when (B)(ii) is valid, we have from (9), $\Omega \gg 1$, and hence

$$\text{(a)} \quad \dot{Y}^{H_2}<\dot{Y}^{HD} \quad \text{or} \quad \dot{Y}^{H_2}>\dot{Y}^{HD},$$

according to whether or not temperature is above or below the optimum. On the other hand (7) predicts

$$\text{(b)} \quad \dot{Y}^{C_2H_6}<\dot{Y}^{C_2H_5D}<\dot{Y}^{C_2H_4D_2}>\dot{Y}^{C_2H_3D_3}>\dot{Y}^{C_2H_2D_4}$$
$$>\dot{Y}^{C_2HD_5}>\dot{Y}^{C_2D_6}$$

above the optimum.

Details of this work will soon appear in J. Research Inst. for Catalysis, Hokkaido University. The writer wishes to express his thanks to Professor Horiuti, Director of the Institute, for his interest in this work.

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[2] Horiuti, Catalyst **2**, 1 (1947).

[3] Horiuti, J. Research Inst. for Catalysis, Hokkaido Univ. (to be published).

[4] Horiuti and Polanyi, Trans. Faraday Soc. **30**, 1164 (1934).

Composition Profiles in Pre-Mixed Laminar Flames*

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To implement a study of temperature and reaction rates of hydrocarbon-air flames a technique has been developed for determining composition profiles through a pre-mixed laminar flame front. By means of a fine probe, samples are taken at various distances normal to the flame front using the center of the luminous zone as a reference surface. These samples are analyzed by means of a rapid-scanning mass spectrometer.[1] Only stable chemical components can be analyzed with the probe technique; therefore, the combustion gases were fed into the ion source of the mass spectrometer in a conventional manner.

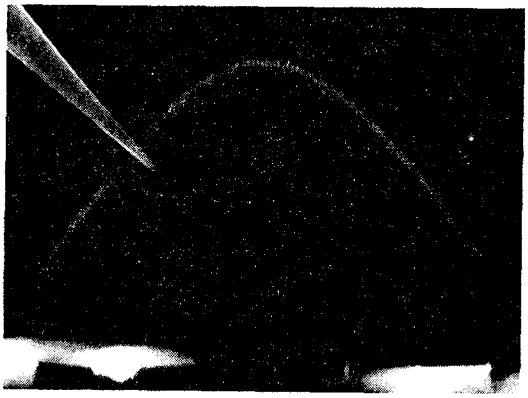

FIG. 1. Photograph of a fused-quartz sampling probe immersed in a propane-air Bunsen flame. (Probe retouched for clarity.)

A half-inch diameter Bunsen burner was used identical to that previously described by Fristrom, Prescott, Neumann, and Avery[2] and was operated in a small chamber exhausted through a critical flow nozzle.

The probes are made of fused quartz and carefully tapered to allow the pressure of the sample to drop rapidly after it enters the probe tip. Probes have been made with the tip as small as 2-microns inside diameter and up to greater than 0.1-mm inside diameter. As it was considered that the larger probes would cause less pyrolysis of the sample these have been used in the preliminary experiments and the sampling system has been designed to handle the flows associated with these larger probes. The probe used for the data herewith was *ca* 0.05-mm inside diameter and

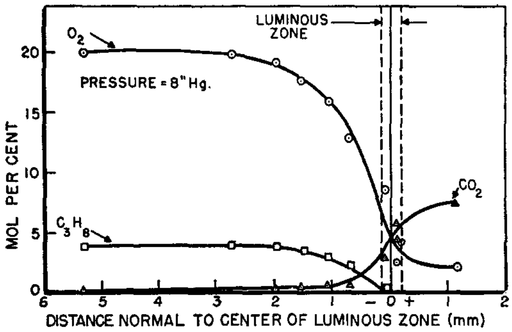

FIG. 2. (a) Mole percent of O_2, CO_2, and C_3H_8 as a function of position in the flame front of a propane-air flame (fuel-to-air ratio 0.93 of the stoichiometric value, pressure 8.0 inches of Hg absolute).

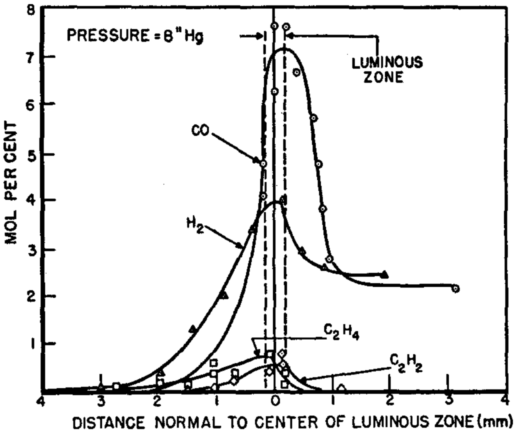

FIG. 2. (b) Mole percent of CO, H_2, C_2H_4, and C_2H_2 as a function of position in the flame front of a propane-air flame (fuel-to-air ratio 0.93 of the stoichiometric value, pressure 8.0 inches of Hg absolute).

0.02-mm wall thickness. From nonviscous, potential flow theory the sampling zone for such a probe is estimated as roughly 1.4 mm in diameter and 0.18 mm in depth. Quenching is accomplished by the rapid drop in pressure of the sample gases which enter the probe tip at sonic speed. The pressure in the sample line is kept at approximately 1 mm Hg, and a fraction of the sample is bled into the mass spectrometer for analysis. Fig. 1 shows a probe in the flame.

Masses from 2 to 100 have been examined, and no appreciable peaks were found above mass 44. Consequently, our analysis was restricted to the mass range 2 to 44. Qualitative tests with heated probes indicated that pyrolysis was negligible in properly drawn probes, and the data shown herewith strengthen the inference that quenching by expansion is effective. A number of runs have been made on a propane-air flame at a pressure of 8 inches of mercury absolute with fuel-to-air ratio 0.93 of the stoichiometric value. Preliminary results are given in Figs. 2 (a) and 2 (b).

In these analyses the following principal components were found: N_2, O_2, A, C_3H_8, C_2H_4, C_2H_2, CO_2, CO, H_2O, and H_2. The present techniques do not permit an accurate determination of H_2O concentration because of adsorption in the sampling system. C_3H_6, C_2H_6, and CH_4 among others were present in quantities less than 0.1-mole percent and are not shown in the accompanying data. To eliminate the effect of temperature on the rate of gas flow into the probe, all the peaks were compared with the argon intensity. The mole fractions were computed from the known concentration (0.90 percent) of argon in the pre-mixed gases using the approximation that the argon mole fraction remained constant, thus neglecting diffusion flows and the change in mole numbers resulting from the combustion reactions.

By passing the gases through a liquid N_2 trap to remove interfering hydrocarbons, H_2, CH_4, and CO were determined with greater accuracy than was possible with unfractionated samples.

These techniques are now being refined, and experiments are under way to obtain the limits of accuracy.

It is hoped that these measurements together with temperature data being obtained on the same system by the particle track method[2,3] will yield quantitative information on the rate and mechanism of reactions in the flame.

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[*] This work was supported by Bureau of Ordnance, U. S. Department of the Navy, under Contract NOrd 7386.

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The Homomolecular Exchange of Nitrogen in a Glow Discharge*†‡

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(Received November 19, 1953)

Recently Johnston and O'Shea[1] reported a study of the exchange reaction between oxygen molecules in which they proposed that reactions of this type be called homomolecular exchange reactions. The present communication reports the discovery of an homomolecular exchange reaction in nitrogen under the influence of an electric glow discharge. In order to study this reaction it was necessary to investigate the possibility of thermal exchange. As expected, no thermal exchange was observed in one month at room temperature or in nineteen hours at 850°C. In the experiments with glow discharge, a mass spectrometer was used to follow the approach to isotopic equilibrium in a mixture of N_2^{28}, N_2^{29}, and N_2^{30} molecules containing fifteen percent nitrogen −15. A nitrogen afterglow was not observed because metal electrodes were used in the reaction cell.

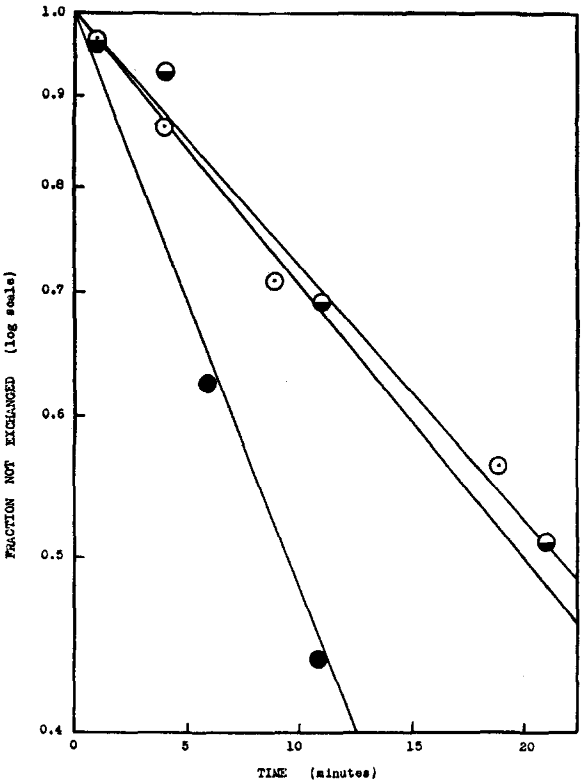

FIG. 1. Homomolecular exchange of N_2 by electric discharge. ⊙ = 2-mm pressure; ● = 4-mm pressure; ◒ = 6-mm pressure.

TABLE I. Actual rates of exchange and effective electron yields.

Pressure	Exchange	Electron current	Yield
2	5.78×10^{15}	7.09×10^{15}	0.82
4	$12.0\ \times10^{15}$	$10.4\ \times10^{15}$	1.15
6	5.37×10^{15}	6.55×10^{15}	0.82

As shown in Fig. 1 first-order rate laws were obtained in glow discharges at pressures of 2, 4, and 6 mm Hg. The half-times at these pressures were 20.0, 9.6, and 21.5 minutes, respectively. The actual rates of exchange, independent of isotopic change, were calculated from these half-times by the equation of Johnston and O'Shea.[1]

An "effective electron yield" was determined for each pressure in units of molecules exchanged per electronic-charge transferred between the electrodes. The actual rates of exchange and the "effective electron yield" are summarized in Table I.

As shown in Table I the "effective electron yield" is essentially unity within experimental error over the pressure range covered and for a range of two-fold in half-time.

If Mitra's[2] dissociative recombination of N_2^+ ions and electrons is responsible for the majority of the charge transfer at the cathode, then recombination of the nitrogen atoms on the metal electrodes or walls would produce exchange with an "effective electron yield" of essentially unity. On the other hand, an atomic chain reaction, $N+N_2$, could reasonably be expected to have an "effective electron yield" from 0 to 10^{+6} depending upon the rate of the chain-breaking reaction and the rate of exchange. The improbability of finding a yield of unity by this mechanism suggests that the experimental value favors the atom-recombination mechanism of exchange.[3]

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[*] This work was supported in part by the U. S. Atomic Energy Commission under contract with Purdue University.

[†] Abstracted from the Master of Science thesis of R. M. Anstett, Purdue University, June 1953.

[‡] Presented before the Physical and Inorganic Division of the 124th Meeting of the American Chemical Society, Chicago, September 11, 1953.

[1] W. H. Johnston and C. J. O'Shea, J. Chem. Phys. 21, 2080 (1953).

[2] F. K. Mitra, Phys. Rev. 90, 516 (1953).

[3] Further work by W. H. Johnston and E. F. Neuzil will be reported soon.