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Equilibrium Atom and Free Radical Concentrations in Carbon Monoxide Flames and Correlation with Burning Velocities

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Calculations have been made of equilibrium concentrations of hydroxyl radicals and of hydrogen and oxygen atoms in moist carbon monoxide flames. Comparison with burning velocities, measured by Jahn by the Bunsen burner method, reveals a close correlation between observed burning velocities and such calculated hydrogen atom concentrations. Only a slight correlation exists with hydroxyl radical concentrations and none at all with calculated oxygen atom concentrations. A theoretical basis for these observations will be presented in a subsequent paper.

INTRODUCTION

WHILE early theories of burning velocity² were based entirely on heat conduction, recent studies^{3,4} have emphasized the importance of diffusion as well. A difficulty in treating the latter has been the evaluation of concentrations of active particles (chain carriers) in the reaction mixture, for kinetic steady state calculations are limited by uncertainty as to the velocities of the elementary reactions which are occurring. There is, however, one set of concentrations which statistical methods allow us to compute with some certainty—namely, the equilibrium concentrations corresponding to the equilibrium flame temperature and over-all composition. It may perhaps be questioned whether such calculations correspond to reality, since combustion may not always proceed to thermodynamic equilibrium; nevertheless, it has seemed worth while to make such calculations and to explore in some well investigated case the possibility that a correlation might exist between these equilibrium concentrations and observed burning velocities.

A particularly suitable example is the combustion of moist carbon monoxide, on which an extensive series of measurements have been performed by Jahn,⁵ using the Bunsen burner

method first developed by Gouy.⁶ Such measurements are open to some question;⁷ however, the method and underlying assumptions are simple and certainly permit an estimate of relative velocities at the very least. Accordingly, we have computed for a number of the mixtures used by Jahn, the equilibrium flame temperatures and the corresponding concentrations of hydroxyl radicals and of hydrogen and oxygen atoms. These have been compared with Jahn's observed burning velocities.

METHOD OF CALCULATION

Equilibrium partial pressures of free radicals in flames can be calculated by use of appropriate equilibrium constants, provided that the flame temperature is known. (The concentrations of oxygen, carbon monoxide, and carbon dioxide, of course, are also assumed to be at equilibrium.) To evaluate this flame temperature a modification of the method of Lewis and von Elbe⁸ has been used, involving a balancing of the heat of reaction to the final products (which will be partly dissociated into atoms and radicals) against the heat required to raise these products to the flame temperature. The flame temperature and the degrees of dissociation of the various product molecules are thus clearly interdependent, and a procedure involving trial and error must be adopted for the calculation.

The equilibrium constants used in the calculations reported in this paper have been taken from

¹ National Research Council Predoctoral Fellow in Chemistry, 1946–1947.

² E. Mallard and H. L. Le Chatelier, *Ann. des Mines* (8) **4**, 274 (1883).

³ B. Lewis and G. von Elbe, *J. Chem. Phys.* **2**, 283 (1934).

⁴ Y. Zeldovich and N. Semenov, *J. Exp. Theoret. Phys. U.S.S.R.* **10**, 1116 (1940). Translation in *N.A.C.A. Tech. Memo. No. 1084* (1946).

⁵ G. Jahn, *Der Zündvorgang in Gasgemischen* (Oldenbourg, Berlin, 1942).

⁶ M. Gouy, *Ann. Chim. Phys.* (5) **18**, 1 (1879).

⁷ B. Lewis and G. von Elbe, *J. Chem. Phys.* **11**, 75 (1943).

⁸ B. Lewis and G. von Elbe, *Phil. Mag.* **20**, 44 (1935).

TABLE I. Free radical concentrations and burning velocities in carbon monoxide flames.

Composition	Flame temperature (calc.) °K	Equilibrium partial pressures of radicals (calc.)			Burning velocity (Jahn) cm/sec.
		P _O atm. × 10 ³	P _{OH} atm. × 10 ⁴	P _H atm. × 10 ⁴	
35% CO, * 8.5% O ₂ , 56.5% N ₂	1730	—	0.016	0.11	25.5
26.5% CO, * 44.1% O ₂ , 29.4% N ₂	2320	1.14	20.6	0.68	29.5
40% CO, ** 12.6% O ₂ , 47.4% N ₂	2320	0.12	3.4	2.5	30
40% CO, * 12.6% O ₂ , 47.4% N ₂	2320	0.11	4.9	3.8	40
40% CO, ** 59.1% O ₂ , 0.9% N ₂	2720	28	56	5.6	48
40% CO, * 24% O ₂ , 36% N ₂	2660	10.5	56	11.6	50.5
45% CO, * 22% O ₂ , 33% N ₂	2710	10.0	58	16.0	57
40% CO, * 59.1% O ₂ , 0.9% N ₂	2720	28	88	9.2	60
60% CO, ** 39.4% O ₂ , 0.6% N ₂	2930	42	86	24	68
50% CO, * 30% O ₂ , 20% N ₂	2810	22	91	24	72
80% CO, ** 19.7% O ₂ , 0.3% N ₂	2880	7.6	39	29	72
60% CO, * 24% O ₂ , 16% N ₂	2850	17.6	90	38	83
60% CO, * 39.4% O ₂ , 0.6% N ₂	2930	42	134	39	93
70% CO, * 24% O ₂ , 6% N ₂	2900	20.3	102	52	98
80% CO, * 19.7% O ₂ , 0.3% N ₂	2860	10.0	78	59	106

* CO contains 1.35% H₂O and 1.5% H₂.** CO contains 1.35% H₂O.

the convenient compilation of Lewis and von Elbe,⁹ except those involving hydroxyl radical. The latter have been recalculated by the authors on the basis of Dwyer and Oldenberg's new value for the heat of dissociation of water into hydroxyl and hydrogen.¹⁰ Heat content functions required in the calculations have been taken from tables prepared at the Bureau of Standards.¹¹

CALCULATIONS FOR CARBON MONOXIDE FLAMES

It is interesting first to consider Jahn's experiments upon the addition of small amounts of hydrogen to moist mixtures of carbon monoxide with air or oxygen.⁵ Jahn observed in each case that such addition caused an increase in burning velocity. Similar increases have been reported by other workers upon the addition of small amounts of water vapor to dry carbon monoxide flames.^{12, 13}

We have calculated equilibrium partial pressures of free radicals for a number of Jahn's mixtures and have found, significantly, that the equilibrium partial pressures of hydroxyl radicals and of hydrogen atoms always increase upon the addition of molecular hydrogen. To take just one example (the figures come from Table I): in a mixture of 60 percent moist carbon monoxide with 39.4 percent oxygen and 0.6 percent nitrogen the equilibrium partial pressure of hydrogen atoms is 2.4×10^{-3} atm.; upon the addition of 1.5 percent of hydrogen to the carbon monoxide this figure rises to 3.8×10^{-3} atm. The corresponding figures for hydroxyl radical concentration are 0.86×10^{-2} and 1.3×10^{-2} atm., respectively. The observed burning velocities are 68 cm/sec. without hydrogen and 93 cm/sec. with hydrogen. It should be noted that the equilibrium partial pressures of oxygen atoms do not undergo important changes upon hydrogen addition.

This series of experiments on the addition of hydrogen is particularly crucial because no variables which can be thought of as directly affecting the burning velocity, other than these free radical concentrations, are appreciably altered by such addition. Thus the flame temperature, when calculated to the nearest 10°, is completely unchanged, and changes in thermal and diffusion properties can be only very slight.

It is clearly desirable to extend these calculations to cover the whole range of moist carbon monoxide flames examined by Jahn. Table I contains a series of such calculations for a variety

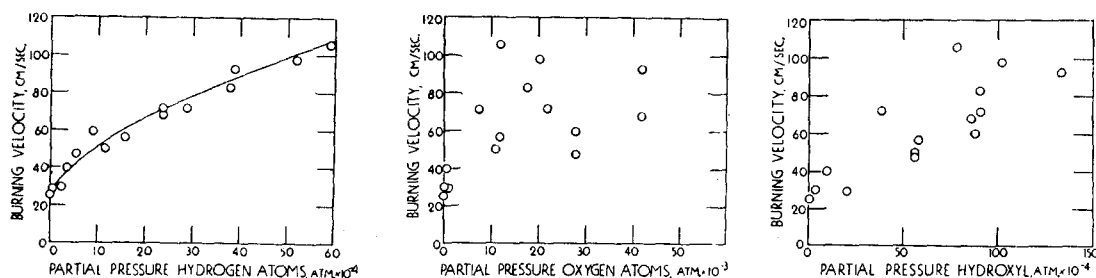


FIG. 1. Correlation between burning velocity and free radical concentrations.

⁹ B. Lewis and G. von Elbe, *Combustion, Flames and Explosions of Gases* (Cambridge University Press, England, 1938), p. 380.

¹⁰ R. J. Dwyer and O. Oldenberg, *J. Chem. Phys.* **12**, 351 (1944).

¹¹ D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer, and F. D. Rossini, *J. Research Nat. Bur. Stand.* **34**, 143 (1945).

¹² L. Ubbelohde and O. Dommer, *J. Gasbel.* **57**, 757, 781 (1914).

¹³ E. F. Fiock and C. H. Roeder, *N.A.C.A. Reports* 532 (1935), 553 (1936).

of mixtures, varying from rich mixtures with only one-half the stoichiometric amount of oxygen to lean mixtures with three times the stoichiometric oxygen content. Moreover, the ratio of oxygen to nitrogen varies from 1:4 to 65:1, and mixtures with and without added hydrogen are included. The last column of Table I contains Jahn's experimental burning velocities, and in Fig. 1 these have been plotted against values of the partial pressures of hydroxyl radicals and of hydrogen and oxygen atoms. It is apparent that no correlation exists between burning velocity and oxygen atom concentration, and a slight one at best between burning velocity and hydroxyl radical concentration. On the other hand, a striking correlation is seen to exist between burning velocity and hydrogen atom concentration.

That such a correlation should exist for hydrogen atom concentration, but not for oxygen atom or hydroxyl radical concentration, is not unexpected. For, if the extent to which free radicals in the flame can be utilized in the combustion process depends upon diffusion—and it is logical to make such a supposition—the effect of hydrogen atoms, because of their very high rates of diffusion, will overshadow that of any of the other radicals. It would further appear that if such a correlation exists in carbon monoxide flames, it should also hold true for pure hydrogen flames. Preliminary calculations show that this is indeed true, and further work on such flames is planned.

Another paper will be presented in the very near future which will suggest a theoretical basis for the results outlined above.

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Theory of Burning Velocity. I. Temperature and Free Radical Concentrations Near the Flame Front, Relative Importance of Heat Conduction and Diffusion¹

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(Received April 21, 1947)

A previous paper having suggested that hydrogen atoms play an important part in combustion, an investigation is made of the relative importance of heat conduction and diffusion in establishing concentrations of hydrogen atoms near the flame front. To do this, differential equations are set up for heat transfer and for material transport. These equations are solved for two typical mixtures, one containing moist carbon monoxide, the other containing hydrogen. It is shown that the temperature falls rapidly as the distance from the flame front increases, and that the local thermal equilibrium concentration of hydrogen atoms, being a negative exponential of that temperature, falls more rapidly still. On the other hand, the local non-equilibrium concentration of hydrogen atoms, which is caused by diffusion from the flame front into unburnt gas, falls only slowly with distance. It is thus concluded that diffusion plays a more important role than heat transfer.

INTRODUCTION

IT has already been suggested by Lewis and von Elbe³ that the diffusion of atoms and free radicals is more important than heat conduction in initiating combustion. This idea received sup-

port in a communication from this laboratory⁴ in which calculations were made of equilibrium atom and free radical concentrations in moist carbon monoxide flames for points at which combustion has proceeded adiabatically to equilibrium. It was shown that there exists a very close correlation between such calculated hydrogen atom concentrations and experimentally

¹ Abstracted in part from a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

² National Research Council Predoctoral Fellow in Chemistry, 1946-47.

³ B. Lewis and G. von Elbe, *J. Chem. Phys.* 2, 537 (1934).

⁴ C. Tanford and R. N. Pease, *J. Chem. Phys.* 15, 431 (1947).