A similar effect was already found in the reduction of nickel oxide with hydrogen.[4] Since in that case it was concluded that the over-all process is determined by hydrogen chemisorption and since it is known from semi-conductivity data[1,2] that on p-type oxides carbon monoxide behaves essentially as an electron donor, it is possible to conclude from the effect of impurities on the activation energy of the oxidation reaction that the interaction of carbon monoxide with the oxide surface is the controlling step in the high temperature interval of the reaction.

A similar conclusion was previously reached on kinetic grounds.[5] This agreement is regarded as supporting evidence for the kinetic scheme pro-posed. The addition of foreign ions into the nickel oxide lattice might modify the concentration and distribution of holes and electrons by suitable changes of the Fermi level of the semi-conductor. This can be related to the experimentally observed effect of additions on the activation energy of heterogeneous processes involving formation and/or destruction of acceptor and donor levels in semi-conductors. Although the effect has been observed so far on the over-all activation energy, it may lead, if substantiated by further experimental work, to a method for controlling, at least qualitatively, the activation energies of heterogeneous processes occurring on semi-conducting materials.

PRINCETON, N. J.

The Effect of Water on the Burning Velocities of Cyanogen–Oxygen–Argon Mixtures[1]

BY RICHARD S. BROKAW AND ROBERT N. PEASE

Burning velocities have been determined for cyanogen–oxygen–argon mixtures containing varying amounts of moisture. The effect of water is explainable on the basis of the Tanford–Pease theory of flame speeds. Experiments with heavy water suggest that the hydroxyl radical is more important than the hydrogen atom in determining the rate of flame propagation.

Tanford and Pease[2] have put forward a theory of burning velocity which assumes that the rate of flame propagation is determined by the rate at which atoms and radicals from the burned gas diffuse into and react with the unburned fuel. In particular they applied their theory to the measurements of Jahn[3] on moist carbon monoxide. In these calculations hydrogen atoms and hydroxyl radicals were the active species considered. Hoare and Linnett[4] have pointed out that it is possible to explain the effect of water or hydrogen on carbon monoxide flame velocities by a thermal theory of flame propagation.

In view of the above, it was felt that it would be desirable to determine the effect of added water on the burning velocity of another hydrogen-free fuel. Cyanogen was selected for these studies, since it is easily prepared, and as it is composed of carbon and nitrogen alone, equilibrium flame temperature calculations are not unduly complicated. Furthermore, the work of Hadow and Hinshelwood[5] shows that water has no effect on the rate of the slow oxidation of cyanogen (apparently a surface reaction).

(1) The work described in this paper was carried out at Princeton University in connection with Contract NOrd 7920 with the United States Naval Bureau of Ordnance, as coördinated by the Applied Physics Laboratory, The Johns Hopkins University, and Contract N6-ori-105 with the Office of Naval Research and Office of Air Research as coördinated by Project Squid, Princeton University. Reproduction in whole or in part permitted for any purpose of the United States Government. We wish to acknowledge the assistance of Dean H. S. Taylor, who has general supervision of this project.

(2) C. Tanford and R. N. Pease, J. Chem. Phys., 15, 861 (1947).

(3) G. Jahn, "Der Zündvorgang in Gasgemischen," Oldenbourg, Berlin, 1942.

(4) M. F. Hoare and J. W. Linnett, J. Chem. Phys., 16, 747 (1948).

(5) H. J. Hadow and C. N. Hinshelwood, Proc. Roy. Soc. (London), A132, 375 (1931).

Experimental

Flame velocities have been determined on a bunsen burner apparatus. Capillary flow meters were used to measure the rates of oxygen and argon flow. In order to conserve cyanogen, this gas was added to the gas stream by mercury displacement from a cylindrical reservoir flask of about 300-cc. capacity. A hydraulic cylinder was used to raise a cylindrical leveling bulb at a uniform rate, controlled by a needle valve on the water line. The travel of the hydraulic cylinder also closed and opened a switch on a Gralab Model No. 201 microtimer which measured the time required to displace a standard volume of gas, and thereby the cyanogen flow rate.

The flames were ignited by means of an induction spark and were stabilized on a 0.806 cm. i.d. Pyrex burner enclosed in a 4-cm. mantle. A flow of dry nitrogen approximately equal to the flow rate through the burner was introduced into the annular space. This helped to sweep out combustion products and aided in stabilizing the flame. Photographs were taken with a Leica camera equipped with a 5-cm. extension tube. The flames are highly luminous so that exposures as fast as $^1/_{800}$ second at f25 on Kodak plus-X film were in some instances used. Burning velocities were determined by considering the flow through a frustum of the cone between the diameters of 0.2 to 0.7 cm. This method, proposed by Dery,[6] eliminates the disturbed areas at the base and tip of the cone. Frustum areas were obtained from enlarged tracings of the flame photographs.

Cyanogen was prepared by thermal decomposition of mercuric cyanide which was first mildly heated *in vacuo* to drive off any moisture which might be present. The cyanogen was passed over magnesium perchlorate and frozen out by liquid nitrogen. It was stored in 3- and 5-liter glass flasks, and could be introduced into the cylindrical reservoir flask by means of a Toepler pump. A sample of cyanogen was analyzed for hydrogen cyanide by the method of Rhodes,[7] and no trace of the latter was found. In addition, vapor pressures at -78, -45 and $-39°$ checked with the values of Perry and Bardwell.[8]

(6) R. J. Dery, see M. E. Harris, J. Grumer, G. von Elbe and B. Lewis, "Third Symposium on Combustion and Flame and Explosion Phenomena," Williams & Wilkins Co., Baltimore, Md., 1949, p. 88.

(7) F. H. Rhodes, J. Ind. Eng. Chem., 4, 652 (1912).

(8) J. H. Perry and D. C. Bardwell, THIS JOURNAL, 47, 2629 (1925).

Water vapor was introduced into either the argon or the oxygen stream by means of a saturator at room temperature. The water concentration was controlled by passing the gas through two brass traps filled with copper shot and immersed in a thermostat.

Argon was obtained from the Matheson Company and oxygen from the American Oxygen Company.

Results and Discussion

A few preliminary experiments on cyanogen–air flames showed that the burning velocities are low (estimated as less than 20 cm./sec.), as may be inferred from examining the burner diameters and flow rates employed by Smithells[9] in his experiments on interconal sampling of cyanogen–air flames. This is somewhat surprising when one considers that the equilibrium flame temperature for the stoichiometric cyanogen–air flame (2600°K.) is about the same as that of the acetylene–air flame (burning velocity ~ 150 cm./sec.), and this again reminds us of the remarkable stability of cyanogen. In order to increase the burning velocities to more conveniently measured values the cyanogen flames studied were burned with an atmosphere composed of 25% oxygen and 75% argon.

The results of experiments with varying amounts of water (expressed as the concentration in the oxygen–argon mixture, $H_2O/O_2 + A$) are shown in Fig. 1. In most of the determinations the oxygen plus argon flow rate was maintained at 30 cc. per second; a few runs (heavy horizontal bars through data points) were run at 40 cc./sec. Mixtures containing more than 20% cyanogen burn smoothly but are blindingly bright due to incandescent carbon formation, so that it is impossible to photograph the inner cone. Flames containing about 18% or more of cyanogen, particularly with the large amounts of water, tended to be polyhedral.

It is seen that water vapor markedly increases the flame speeds of these mixtures. It might be argued that the presence of water vapor is necessary to permit the combustion of the leaner mixtures to carbon dioxide, as shown by the experiments of Berl and Barth.[10] However, in the vicinity of 20% C_2N_2 there is still a pronounced effect of water on the burning velocity, although here the combustion products will be carbon monoxide and nitrogen regardless of the moisture content (at 11.11% C_2N_2 stoichiometry gives CO_2 and nitrogen as products; at 20% C_2N_2 carbon monoxide and nitrogen are formed).

The Tanford–Pease equation[2] was applied in the following way. The equation can be written as

$$u = \left[\sum_i (k_i C p_i D_i)/Q \right]^{1/2} \tag{1}$$

where

u = burning velocity
C = concn. of fuel in molecules/cc. (a mean value over the combustion zone)
p_i = mole fraction of the ith active species at the flame front.
D_i = the diffusion coefficient into the unburned gas for ith active species
k_i = the rate constant for the reaction of the ith active species
Q = mole fraction of potential combustion product

(9) A. Smithells and F. Dent, *J. Chem. Soc.*, **65**, 603 (1892).

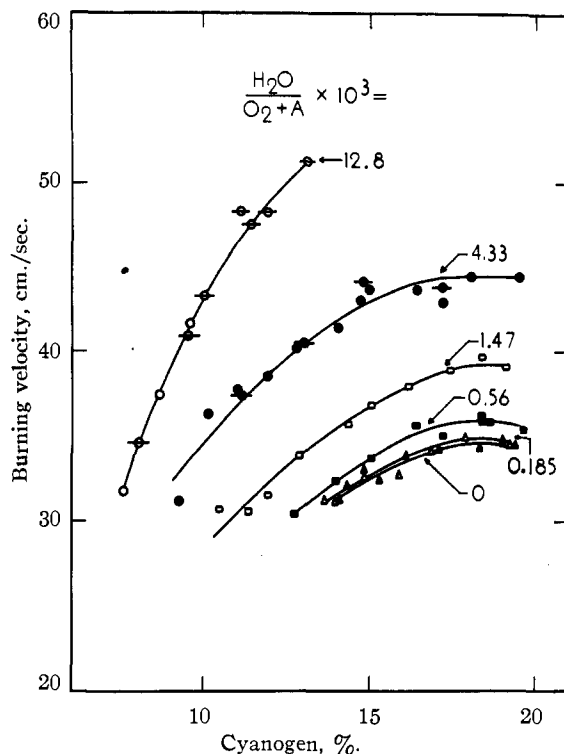(10) E. Berl and K. Barth, *Z. physik. Chem., Bodenstein-Festband* 211 (1931).

Fig. 1.—Burning velocities of cyanogen–oxygen–argon mixtures with added water $[O_2/(O_2 + A) = 0.25]$.

Equation (1) may be rewritten in the form

$$u^2 = \sum_i a_i p_i = a_H p_H + a_{OH} p_{OH} + \sum_j a_j p_j \tag{2}$$

The equilibrium concentrations of the active species other than hydrogen atoms and hydroxyl radicals (*e.g.*, oxygen atoms, cyanide radicals) will not be greatly affected by the addition of water vapor. In Table I equilibrium concentrations for various mixtures are given.

These have been calculated using equilibrium constants tabulated by Lewis and von Elbe[11] and other necessary thermochemical data from the Bureau of Standards publications.[12] Since at a fixed percentage of cyanogen the ratio of H to OH remains almost constant as the water concentration is varied, we may rewrite equation (2)

$$u^2 = [a_H(p_H/p_{OH}) + a_{OH}]p_{OH} + \sum_j a_j p_j \tag{3}$$

$$\cong b p_{OH} + u_0^2$$

where b and u_0 are approximately constant (u_0 corresponds to the flame speed without added water).

Therefore graphs of the square of the burning velocity against the hydroxyl concentration at constant richness should be linear. Such plots are shown in Fig. 2 and, indeed, excellent straight lines are obtained. If it be assumed that the coefficients a_H and a_{OH} are independent of composi-

(11) B. Lewis and G. von Elbe, "Combustion, Flames and Explosions of Gases," Academic Press, Inc., New York, N. Y., 1951, pp. 742–743.

(12) "Selected Values of Properties of Hydrocarbons," Circular of the National Bureau of Standards C 461; "Selected Values of Chemical Thermodynamic Properties," Circular of the National Bureau of Standards 500, U. S. Government Printing Office.

TABLE I

EQUILIBRIUM FLAME TEMPERATURES AND RADICAL CON-
CENTRATIONS IN 250_2:75A MIXTURES

$\frac{H_2O}{O_2 + A} \times 10^3$	Flame temp., °K.	H	Concn., atm. $\times 10^4$ OH	O
		11.11% C_2N_2		
12.8	2910	34.4	59.4	183.6
4.33	2934	17.45	29.0	200.5
1.47	2945	7.63	12.32	209.3
		13% C_2N_2		
12.8	2994	49.5	55.5	193.5
4.33	3020	23.8	25.2	215.8
1.47	3031	9.97	10.31	225.3
0.56	3036	4.12	4.23	229.4
		16% C_2N_2		
4.33	3138	36.0	17.13	190.2
1.47	3156	13.78	6.30	201.4
0.56	3163	5.48	2.47	206.2
0.185	3166	1.85	0.829	208.4
0	3168	0	0	209.4
		19% C_2N_2		
4.33	3284	48.7	5.02	88.4
1.47	3319	17.80	1.62	92.0
0.56	3331	6.94	0.598	92.7
0.185	3336	2.21	0.186	92.9
0	3339	0	0	93.0

tion (this assumption is almost certainly not valid since rate constants are markedly temperature dependent), then a plot of the slopes of the lines of Fig. 2 $(a_H(p_H/p_{OH}) + a_{OH})$ against the ratio of the hydrogen atom and hydroxyl radical concentrations should yield a straight line of slope a_H and intercept a_{OH}. If this be done, a reasonably good straight line is obtained and the ratio a_{OH}/a_H is found to be roughly 1.4; that is to say, the hy-
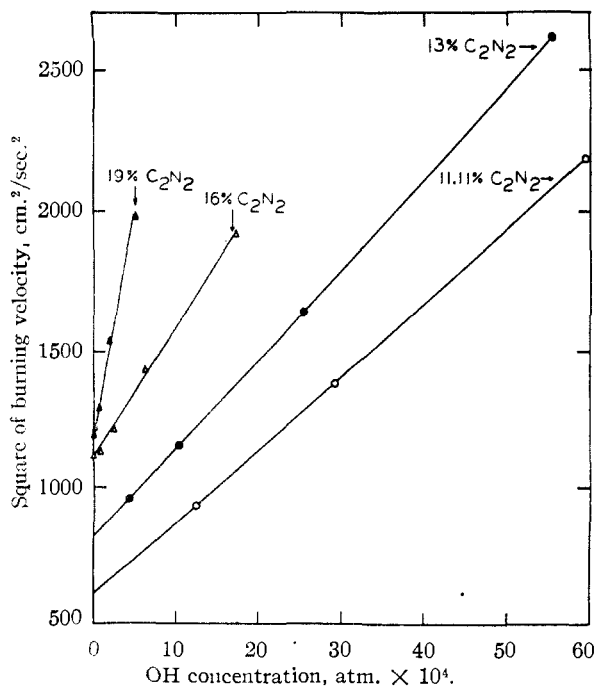

Fig. 2.—Plots of the square of the burning velocity against equilibrium hydroxyl radical concentrations.

droxyl radical appears to play a more important part than the hydrogen atom, despite its markedly lower diffusivity (about $1/4$ that of the hydrogen atom).

In order to check the relative importance of H and OH in cyanogen combustion, experiments on the burning velocity of cyanogen with added heavy water (D_2O) were made. Unfortunately these flames were markedly less stable; in many instances the flames disappeared shortly after the exposures were made. Therefore the data exhibited in Fig. 3 show considerable scattering and should not be regarded as accurate.
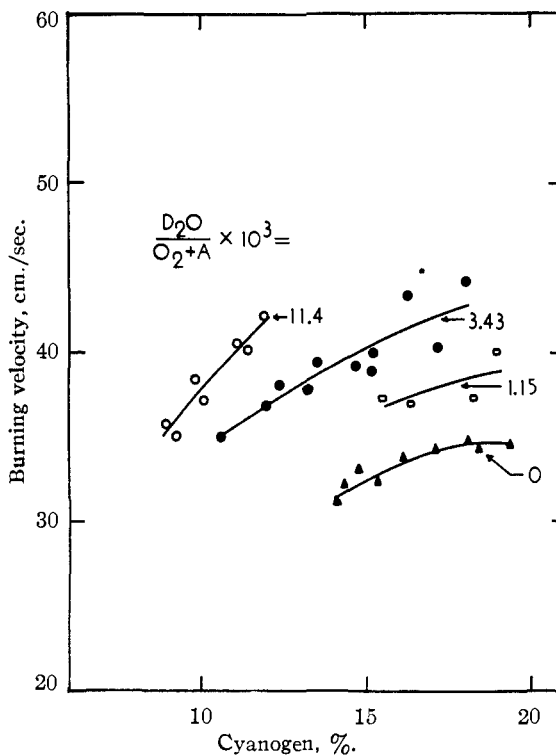

Fig. 3.—Burning velocities of cyanogen–oxygen–argon mixtures with added heavy water $[O_2/(O_2 + A) = 0.25]$.

Equilibrium flame temperatures and compositions for the mixtures studied have been calculated, adjusting equilibrium constants by the relationships

$$\frac{[D]^2[H_2O]}{[H]^2[D_2O]} =$$

$$2.585 \frac{1 - e^{-1744/T}}{1 - e^{-2380/T}} \frac{1 - e^{-3969/T}}{1 - e^{-5504/T}} \frac{1 - e^{-4149/T}}{1 - e^{-5662/T}} e^{-1842/T}$$

$$\frac{[D][OH]}{[H][OD]} = 1.374 \frac{1 - e^{-3907/T}}{1 - e^{-5366/T}} e^{-729.6/T}$$

$$\frac{[D]^2[H_2]}{[H]^2[D_2]} = 1.414 \frac{1 - e^{-4488/T}}{1 - e^{-6340/T}} e^{-926/T}$$

and assuming the heats of formation at 298.1°K. for OD, D and D_2O are +9.502, +52.982 and −59.5628 kcal., respectively. For similar amounts of H_2O and D_2O, flame temperatures were found to be the same within one degree in the extreme cases. The results of these calculations are contained in Table II.

In Table III comparison is made between burning velocities and calculated OD concentrations for

TABLE II

EQUILIBRIUM FLAME TEMPERATURES AND RADICAL CONCENTRATIONS

$\frac{D_2O}{O_2 + A} \times 10^3$	Flame temp., °K.	Concentrations, atm. × 10^4 D	OD	O
		11.11% C_2N_2		
11.4	2913	30.4	55.7	185.9
3.43	2938	14.17	24.6	203.0
		13% C_2N_2		
3.43	3023	19.30	21.54	218.7
		16% C_2N_2		
3.43	3143	28.7	14.27	193.1
1.15	3158	10.70	5.14	203.0
		19% C_2N_2		
3.43	3295	39.1	4.09	89.7
1.15	3323	13.81	1.294	92.3

mixtures with added heavy water. These figures are compared with corresponding values for OH concentrations to give the same burning velocity with ordinary water, read from Fig. 2. It is seen that the OH and OD appear to be about equally effective; in other words $a_{OD} \cong a_{OH}$. Apparently hydrogen and deuterium atoms do not make as great a contribution to the flame speeds; if they did we would not anticipate the agreement shown in Table III since H and D have different diffusion coefficients, such that $a_H \cong 1.4\ a_D$. However, we would like to emphasize again that the data on mixtures with heavy water are somewhat uncertain.

TABLE III

% C_2N_2	Burning velocity, cm./sec.	Calcd. OD concn., atm. × 10^4	OH concn. for same burning velocity (from fig. 2) (atm. × 10^4)
11.11	40.3	55.7	38.3
11.11	35.7	24.6	25.2
13	38.2	21.5	19.8
16	41.2	14.3	12.4
16	37.2	5.1	5.7
19	(43.5)	4.1	4.1
19	38.9	1.3	1.8

That the hydroxyl radical is present in moist cyanogen flames is shown by the spectroscopic studies of Pannetier and Gaydon,[13] who demonstrated that while the dry cyanogen flame shows only the spectra of C_2 and CN radicals, with water present OH, NH and CH are observed. Possibly non-equilibrium concentrations of NH and CH could also serve as active particles; it would seem likely that their concentrations would be related to the initial water concentrations in a manner similar to the hydroxyl radical.

(13) G. Pannetier and A. G. Gaydon, *Compt. rend.*, **225**, 1300 (1947); G. Pannetier, *Rev. inst. Franc. petrole*, **4**, 418 (1949).

PRINCETON, NEW JERSEY

Anion Exchange Studies. V. Adsorption of Hydrochloric Acid by a Strong Base Anion Exchanger[1,2]

BY KURT A. KRAUS AND GEORGE E. MOORE

The adsorption of HCl by the "strong base" anion exchange resin Dowex-1 was determined in the concentration range 0.002 to 16 molal HCl for the aqueous phase. From these data and measurements of the water content of the resin, the activity coefficients ($\gamma_{\pm HCl}$) of HCl in the resin phase were calculated, and it was found that log $\gamma_{\pm HCl}$ increases linearly with the hydrochloric acid molality of the resin phase.

It has been demonstrated in a series of earlier papers that a number of metals can be strongly adsorbed by anion exchange resins from relatively concentrated hydrochloric acid solutions. These observations focused attention on the behavior of the resin in concentrated electrolytes. Of particular interest is the extent of electrolyte uptake by the resin since it, together with the capacity of the resin, determines the concentration of chloride ions in the resin phase, a variable which appears in the expressions for the adsorption equilibria.

Until relatively recently it was generally assumed that when "strong base" (or "strong acid") ion exchange resins are immersed in electrolyte solutions, little adsorption of the electrolyte as a whole takes place. Thus one expected, for example, that a cation exchanger immersed in sodium chloride solutions would contain few chloride ions and a "strong base" anion exchanger immersed in hydrochloric acid solutions would contain few hydrogen ions. In recent years, however, it was shown that both cation and anion exchangers[3-7] can adsorb considerable quantities of electrolyte if immersed in moderately concentrated solutions and that this adsorption increases with the concentration of electrolyte in the aqueous phase. In most of this work, it was assumed that this electrolyte uptake is closely related to a Donnan equilibrium.

A series of experiments has been carried out which was designed to determine this electrolyte uptake with hydrochloric acid (0.002 to 12 M HCl) for the resin used in the earlier anion exchange studies

(1) This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) Previous paper, G. E. Moore and K. A. Kraus, THIS JOURNAL, **74**, 843 (1952).

(3) W. C. Bauman and J. Eichhorn, *ibid.*, **69**, 2830 (1947).

(4) W. J. Argersinger, Jr., and A. W. Davidson, *J. Phys. Chem.*, **56**, 92 (1952).

(5) J. T. Clarke, J. A. Marinsky, W. Juda, N. W. Rosenberg and S. Alexander, *ibid.*, **56**, 100 (1952).

(6) K. W. Pepper, D. Reichenberg and D. K. Hale, unpublished results reported by K. W. Pepper at the 1951 Gordon Research Conference on Ion Exchange.

(7) H. P. Gregor, THIS JOURNAL, **73**, 642 (1951).