

# COMBUSTION OF HYDROGEN AND OXYGEN WITH AMMONIA AND NITROUS OXIDE—LAMINAR FLAME SPEEDS AND FLAMMABILITY LIMITS AT LOW PRESSURE FOR TERNARY MIXTURES

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Flame speeds relative to the burnt gas ( $S_b$ ) and composition limits of flammability have been measured at sub-atmospheric pressure for the ternary systems  $H_2 + O_2 + NH_3$  and  $H_2 + O_2 + N_2O$ , and flame speeds for some mixtures of  $H_2$  and  $O_2$  with  $N_2$ . In the  $H_2 + O_2 + NH_3$  system, the flammability limits were close to those predicted by the Le Chatelier rule. Flame speed contours on a triangular diagram reflected the form of the limits. In the  $H_2 + O_2 + N_2O$  system, lean mixtures effectively obeyed the Le Chatelier rule, whereas the region of flammability for rich mixtures was conspicuously wider than predicted. The composition dependence of the flame speed showed anomalous behaviour, nitrous oxide and oxygen assisting one another in the combustion of hydrogen. The fastest flame speed occurred in a mixture with a composition 58 per cent  $H_2$  + 12 per cent  $O_2$  + 30 per cent  $N_2O$ . For ternary mixtures containing ammonia or nitrous oxide, excess of either reactant did not survive the flame, but was decomposed into its constituent elements.

Adiabatic flame temperatures and equilibrium compositions of burnt gases were calculated for stoichiometric mixtures and values of the burning velocity relative to unburnt gas ( $S_u$ ) were derived, allowing comparisons with other work at atmospheric pressure, and hence estimates for the overall kinetic order  $n$  to be made. The burning velocities of binary  $H_2 + O_2$  mixtures decreased as the pressure diminished, leading to a value for  $n$  of ca. 2.5. For the binary systems  $NH_3 + O_2$  and  $H_2 + N_2O$  and ternary mixtures with a composition 30 per cent  $H_2$  + 30 per cent  $O_2$  + 40 per cent  $NH_3$ , burning velocities showed little dependence on pressure, indicating an overall kinetic expression of second order.

## Introduction

THERE have been many studies of the combustion of mixtures of hydrogen and oxygen<sup>1</sup>. The most important features of the detailed mechanism are now well established and the properties of hydrogen plus oxygen flames can be interpreted in terms of them. There are, however, few reports of systematic studies of the burning of hydrogen and oxygen with a third constituent (other than those in which the third constituent is inert). The present work is concerned with the measurement of flame speeds and composition limits of flammability at low pressures for such mixtures where the third constituent is another fuel or oxidant.

By studying ternary systems, the effects of interactions between two simultaneous combustion processes are revealed. The simplest behaviour these systems can show is found when the flame speed and final flame temperature vary

monotonically as one constituent replaces the other of the same type (e.g. fuel 1 replaces fuel 2 in a fuel 1 + fuel 2 + oxidant system). In binary systems, the maximum flame speeds and temperatures generally occur in mixtures of nearly stoichiometric composition, and similar behaviour is expected for ternary systems. Similar expectations apply to the composition limits of flammability. Suppose composition limits are represented on a triangular diagram. If the rich (or lean) limits in ternary mixtures lie always along lines joining the two rich (or lean) limits of the binary systems, the ternary system is said to obey Le Chatelier's<sup>2</sup> rule. This 'ideal' behaviour is common, surprisingly so since systems displaying it are behaving as if the combustion processes which occur in the two binary systems, although proceeding simultaneously, have no effect on one another. Small deviations from ideality can often be attributed

to differences in the physical properties of the reactants, but the explanation of marked deviations must be sought in special features of the flame chemistry. Of the systems studied here, one ( $\text{H}_2 + \text{O}_2 + \text{N}_2\text{O}$ ) shows non-ideal behaviour, the explanation of which must be sought in terms of the flame chemistry.

In the present work, flame speeds and composition limits of flammability have been determined for the systems  $\text{H}_2 + \text{O}_2 + \text{NH}_3$  and  $\text{H}_2 + \text{O}_2 + \text{N}_2\text{O}$ ; in addition, the flame speeds have been measured for a few stoichiometric mixtures of  $\text{H}_2 + \text{O}_2 + \text{N}_2$ . The measurements of burning velocity ( $S_b$ ) relative to the burnt gas have been made in a closed vessel at low pressure ( $P_U = 70$  mm of mercury) with an initial temperature of  $60^\circ\text{C}$ . This permits direct comparison to be made with our recent work<sup>3-5</sup> on related binary and ternary systems containing ammonia and hydrazine. The experimental method has several other advantages over burner methods. Smaller amounts of fuels are consumed; the problems of accurately metering fuels are avoided. It allows easy control of initial conditions of temperature and pressure, and has the added advantage that flame curvature is considerably less than in burner experiments.

There are some references to previous work on these ternary systems. Flame speeds have been reported for the  $\text{H}_2 + \text{O}_2 + \text{NH}_3$  system over a limited composition range by Ausloos and van Tiggelen<sup>6</sup> and by Murray and Hall<sup>7</sup>. Flammability limit measurements have been made by Jorissen and Ongkiehong<sup>8</sup> and by Partington and Prince<sup>9</sup>. Also Fenimore and Jones<sup>10</sup> have investigated the reactions occurring in  $\text{H}_2 + \text{O}_2 + \text{NH}_3$  flames. For the  $\text{H}_2 + \text{O}_2 + \text{N}_2\text{O}$  system there appear to be no previous reports of flame speeds or flammability limits, although Fenimore and Jones<sup>11</sup> have studied some of the elementary reactions occurring in  $\text{H}_2 + \text{N}_2\text{O}$  flames.

### Experimental

#### Materials

Hydrogen, oxygen, ammonia and nitrous oxide and nitrogen were taken from cylinders. Ammonia and nitrous oxide were fractionated *in vacuo*, using liquid nitrogen as refrigerant.

#### Apparatus and procedure

**Measurement of flame speeds**—Flame speeds were measured by a constant volume bomb technique; details of the method have been given previously<sup>3</sup>. The combustion vessel was a squat cylinder (21 cm long, 21 cm i.d.) with plate glass end windows. Tungsten electrodes (1 mm diameter) with rounded tips projected horizontally from opposite sides of the vessel, forming a spark gap of 4.4 mm. The vessel was connected by conventional vacuum line to storage bulbs and manometer, and the whole could be evacuated to  $10^{-4}$  mm of mercury between measurements.

As in previous work, the combustion vessel was maintained at  $62^\circ \pm 2^\circ\text{C}$  by an air thermostat. This temperature prevents condensation of water vapour, and allows direct comparison with the previous work<sup>3,4</sup> on related systems. The constituents of ternary mixtures were admitted separately to the combustion vessel and allowed to mix for about 30 min. A total pressure of 70 mm of mercury was used throughout. Initial and final pressures were measured for all mixtures. Duplicate experiments were performed.

The movement of the flame was followed by a Schlieren technique, using a rotating drum camera. The flame progress was recorded as a V-shaped trace. Flame speeds were determined from the slopes of the photographic record at a point corresponding to a flame diameter of 6 cm. At this point, for most mixtures the flame was travelling at constant velocity; for some rich mixtures, however, the flame was still accelerating at this point, and measurements were then made at a slightly greater flame diameter, when constant velocity had been reached. Under these conditions, the observed flame speed is very close to the burning velocity ( $S_b$ ). Their reproducibility of measurement is two per cent in the most favourable cases and up to five per cent for flames with long acceleratory periods.

Triangular diagrams have been drawn showing contours of constant  $S_b$  against composition. To enable easy construction of these diagrams, the flame speeds were determined in sets. For all the mixtures in one set, the mole fraction of one constituent ( $x_1$ ) was fixed, while the other two ( $x_2$  and  $x_3$ ) were varied. From a graph of  $S_b$  against  $x_2$ , the compositions can be found for

particular values of  $S_B$  (500, 1000, 2000 cm sec<sup>-1</sup>, etc.). By giving  $x_1$  a different value in each set, the whole ternary system can be studied. Except at the maximum of the  $S_B$  versus  $x_2$  curve, the compositions could be located to one per cent.

**Determination of flammability limits**—The composition limits of flammability for upward propagation at 50 mm and 70 mm of mercury were determined in a vertical tube (60 cm long; 7.5 cm diameter). An inductive spark passing between tungsten electrodes was used as the ignition source. The spark gap (11 mm wide) was located 6 cm above the base of the tube. Mixtures were made in a 10 litre bulb, the composition being controlled manometrically. The mean of the compositions of the last mixture to ignite and the first which failed to ignite was taken as the limit. In this context, ignition was deemed to have occurred when the flame travelled the whole length of the tube. For a few rich mixtures a discharge of 20 to 25 sec was necessary before propagation occurred. The flames of  $H_2 + O_2$  mixtures were invisible, but often accompanied by an audible 'click'; a change in pressure showed if ignition had occurred.

**Calculations of flame temperatures and burnt-gas composition**—The method of Damköhler and Edse<sup>12</sup> was used for these calculations. The thermodynamic properties required were taken from standard compilations<sup>13,14</sup>.

## Results

### $H_2 + O_2 + NH_3$ system

**Composition limits of flammability**—The flammability limits for the combustion of  $H_2 + NH_3$ , supported by  $O_2$  were measured at 20°C and sub-atmospheric pressure (50 and 70 mm of mercury) and the results are displayed in Figure 1.

At 70 mm total pressure, the rich limits for the two binary mixtures occurred at 87.4 per cent  $H_2$  and 70.5 per cent  $NH_3$ . At 50 mm of mercury the values were 81 and 63 per cent. For ternary mixtures at 70 mm of mercury, the flammability limit essentially obeyed the Le Chatelier<sup>2</sup> rule over most of the composition range. The region of flammability narrowed with the addition of the last 15 per cent  $NH_3$ . The limit at 50 mm of mercury showed greater deviation from Le Chatelier behaviour. However, these deviations

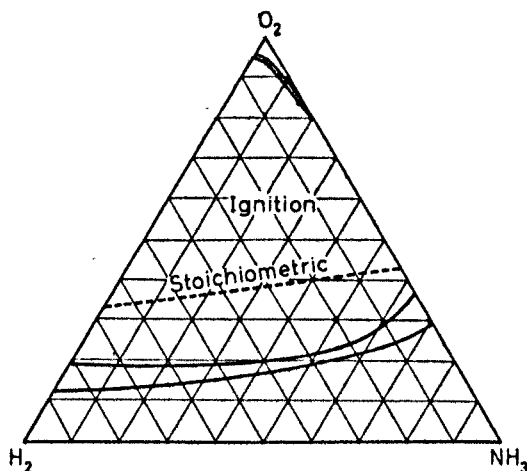


FIGURE 1. Composition limits of flammability at sub-atmospheric pressures for ternary mixtures of  $H_2 + O_2 + NH_3$ . (Outer lines refer to 70 mm pressure and inner to 50 mm of mercury. Dashed line joins all stoichiometric compositions.)

can probably be accounted for by differences in the physical properties of hydrogen and ammonia.

Near the rich limit,  $H_2 + O_2$  flames were invisible, but often accompanied by an audible 'click'. Ternary mixtures burned with very fast flames, reddish in colour. For  $NH_3 + O_2$  mixtures near the rich limit, prolonged sparking with high energy was needed before ignition occurred.

The lean limits for the binary systems occurred at 4 per cent  $H_2$  and 16.5 per cent  $NH_3$  at 70 mm, and 5 per cent and 18.5 per cent at 50 mm of mercury. For ternary mixtures, the flammability region was slightly broader than predictions based on the Le Chatelier<sup>2</sup> rule would expect.

Near the lean limit, slow flames were propagated (rate of travel ca. 20 cm sec<sup>-1</sup>), and these flames were blue-green in colour. Partial ignition often occurred in mixtures with compositions outside the lean limit.

**Laminar flame speeds: effect of composition**—Figure 2 shows the results of the dependence of flame speeds ( $S_B$ ) on composition at 70 mm of mercury initial pressure and  $62^\circ \pm 2^\circ C$  initial temperature.

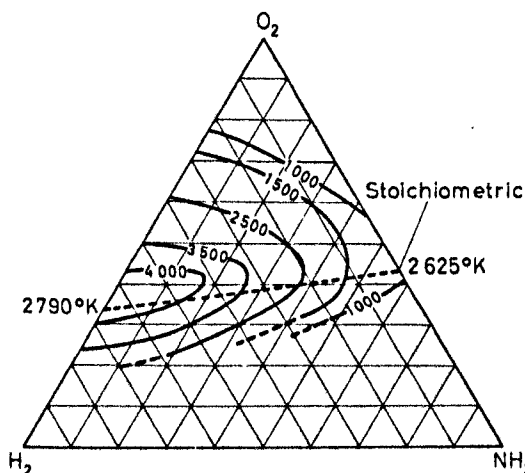


FIGURE 2. Dependence of burning velocity ( $S_B$ , cm sec $^{-1}$ ) on composition in ternary mixtures of  $H_2 + O_2 + NH_3$ : contours join compositions giving equal values of  $S_B$ . (Dashed line joins all stoichiometric compositions.)

Flame speeds fell continuously as  $H_2$  was replaced by  $NH_3$ . The fastest flame ( $S_B = 4180$  cm sec $^{-1}$ ) occurred in a slightly fuel-lean  $H_2 + O_2$  mixture, containing 63 per cent  $H_2$ . At the other extreme ( $NH_3 + O_2$ ), the fastest flame ( $S_B = 1250$  cm sec $^{-1}$ ) also occurred in a lean mixture (53 per cent  $NH_3$ ). The flame speeds for the two stoichiometric mixtures were 4100 cm sec $^{-1}$  and 1100 cm sec $^{-1}$ . For ternary mixtures, flame speeds fell off on either side of the line joining the two maxima. On the lean side of stoichiometric, this decrease occurred relatively slowly, but was much more rapid for rich mixtures.

#### $H_2 + O_2 + N_2O$ system

**Composition limits of flammability**—The flammability limits for this system at 50 mm and 70 mm of mercury are shown in Figure 3. Several qualitative observations can be made about the flames. Near the rich limit,  $H_2 + N_2O$  flames were vigorous, instantaneous and accompanied by a bright flash. In ternary mixtures near the rich limit, flames were also very fast, but orange in colour. Near the lean limit, on the other hand, very slow flames could be propagated, and these flames were generally yellow-green in colour. Partial ignition often occurred in mixtures outside the lean limit.

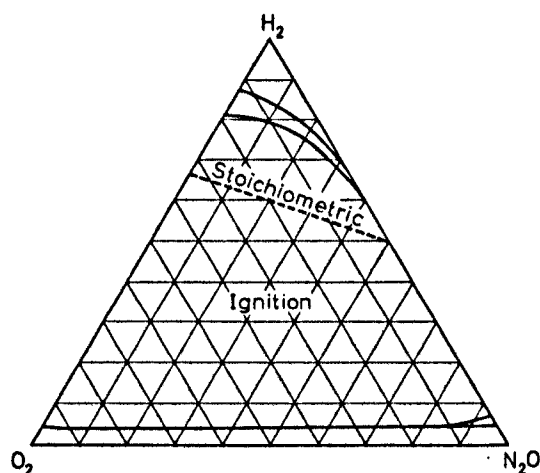


FIGURE 3. Composition limits of flammability at sub-atmospheric pressures for ternary mixtures of  $H_2 + O_2 + N_2O$ . (Outer lines refer to 70 mm pressure and inner to 50 mm of mercury. Dashed line joins all stoichiometric compositions.)

In the binary  $H_2 + O_2$  system, limits were observed at 4.5 per cent and 87.4 per cent  $H_2$  at 70 mm and 4.5 per cent and 81.4 per cent  $H_2$  at 50 mm of mercury. For binary  $H_2 + N_2O$  mixtures, the limits occurred at 4.5 and 68.5 per cent  $H_2$  at 70 mm and 7.0 and 62 per cent  $H_2$  at 50 mm of mercury. The rich limit line in the ternary mixtures was bowed, the limit being wider when mixed oxidants were present. At the lean limit, the region of flammability broadened very slightly on addition of the first few per cent of nitrous oxide and then remained constant, until the last 20 per cent of oxygen was replaced by nitrous oxide, when it narrowed slightly again. With mixed oxidants containing up to 80 per cent nitrous oxide, the difference between the limits at 70 mm and 50 mm of mercury was less than ca. 0.5 per cent and was certainly inside the experimental error. At the lean limit, the Le Chatelier<sup>2</sup> rule was substantially obeyed.

**Laminar flame speeds: effect of composition**—The results are shown in Figure 4. For the  $H_2 + N_2O$  binary system, the fastest flame ( $S_B = 3470$  cm sec $^{-1}$ ) occurred in a slightly rich mixture, containing 53 per cent  $H_2$ . For the stoichiometric mixture,  $S_B = 3440$  cm sec $^{-1}$ . For the  $H_2 + O_2$  system, the maximum speed was 4180 cm sec $^{-1}$  at 63 per cent  $H_2$ . Faster

flames occurred when both oxidants were present together than when either was present alone. The maximum flame speed for the ternary system was  $5000 \text{ cm sec}^{-1}$  and was found for a composition of 58 per cent  $\text{H}_2$  + 12 per cent  $\text{O}_2$  + 30 per cent  $\text{N}_2\text{O}$ .

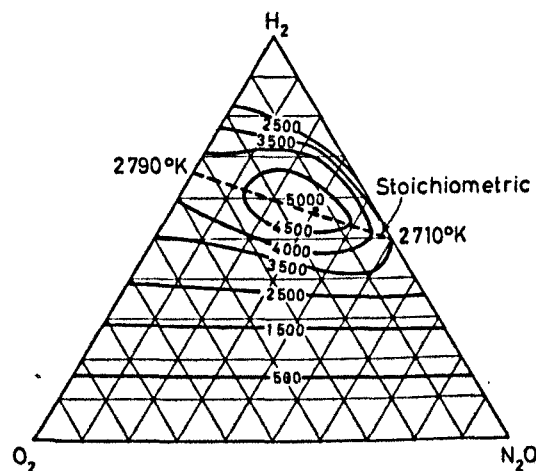


FIGURE 4. Dependence of burning velocity ( $S_b$ ,  $\text{cm sec}^{-1}$ ) on composition in ternary mixtures of  $\text{H}_2 + \text{O}_2 + \text{N}_2\text{O}$ : contours join compositions giving equal values of  $S_b$ . (Dashed line joins all stoichiometric compositions.)

In increasingly rich mixtures, particularly those with less than about ten per cent oxygen, flame speeds decreased very rapidly. In lean mixtures, speeds decreased relatively slowly with departures from stoichiometric, and for mixtures with up to ca. 30 per cent  $\text{H}_2$ , the flame speed was independent of the relative proportions of oxygen and nitrous oxide.

In rapidly burning  $\text{H}_2 + \text{N}_2\text{O}$  mixtures a turbulence resulted as the flame impinged on the vessel walls. This turbulence also occurred with mixtures containing 10 per cent  $\text{O}_2$ , but had disappeared in mixtures with 20 per cent  $\text{O}_2$ .

In addition, flame speeds were determined for two mixtures, with compositions  $2\text{H}_2 + \text{O}_2$  and  $6\text{H}_2 + 3\text{O}_2 + \text{N}_2\text{O}$ , to which small amounts (up to one per cent) of nitric oxide had been added. The flame speeds decreased as the NO concentration increased. For the  $2\text{H}_2 + \text{O}_2$  mixture the flame speed was reduced by ca. 2.5 per cent with 0.5 per cent nitric oxide and

ca. 3 per cent with 1 per cent nitric oxide. For the  $6\text{H}_2 + 3\text{O}_2 + \text{N}_2\text{O}$  mixture, addition of 0.5 per cent nitric oxide lowered the flame speed by about ten per cent.

### $\text{H}_2 + \text{O}_2 + \text{N}_2$ system

*Laminar flame speeds: effect of composition*—Flame speeds were measured for a few stoichiometric mixtures of  $\text{H}_2 + \text{O}_2$ , diluted with varying amounts of  $\text{N}_2$ , at a total pressure of 70 mm of mercury. The results are shown in Figure 5, where they are compared with the flame speeds of stoichiometric mixtures of  $\text{H}_2 + \text{O}_2$  with added  $\text{NH}_3$  and  $\text{N}_2\text{O}$ . With the addition of  $\text{N}_2$ ,

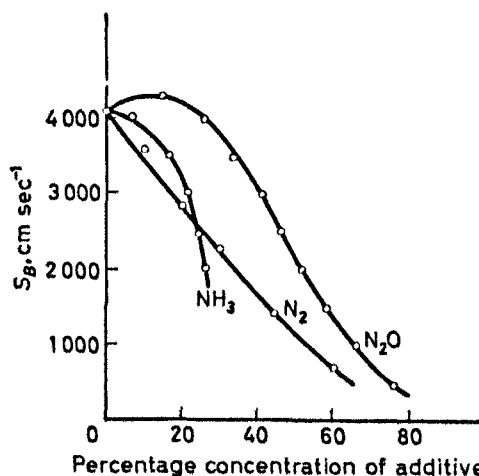


FIGURE 5. Effects of additives on the flame speed in stoichiometric mixtures of hydrogen with oxygen: flame speed, at a total pressure of 70 mm of mercury, as a function of the additive concentration

the flame speeds decreased smoothly from the value of  $4100 \text{ cm sec}^{-1}$  (when no  $\text{N}_2$  was present) to  $700 \text{ cm sec}^{-1}$  with 60 per cent  $\text{N}_2$ . Mixtures with more than 60 per cent  $\text{N}_2$  were not burned, as the burning velocities of the  $\text{H}_2 + \text{O}_2 + \text{N}_2$  system were measured solely to act as a 'neutral' standard with which to compare the behaviour of a second fuel or second oxidant.

### Flame temperatures, burnt-gas composition, and flame speeds relative to unburnt gas

To convert the present results to flame speeds relative to the unburnt gas ( $S_u$ ), it is necessary to

calculate the final flame temperature and the ratio of the numbers of moles of burnt and unburnt gas. In order for these calculations to be valid, complete combustion must occur. Experimental values of the pressure change accompanying combustion are in fairly close agreement with the calculated values, assuming maximum conversion to the products  $N_2$  and  $H_2O$ , and the decomposition of excess reactants,  $NH_3$  and  $N_2O$ . This evidence supports the idea that complete combustion occurs. For stoichiometric mixtures, near-equilibrium conditions are obtained, and calculations can be performed with confidence. In mixtures far from stoichiometric, however, non-equilibrium conditions render such calculations unreliable.

Calculations were performed for stoichiometric mixtures in all three systems. The final flame temperatures and equilibrium compositions of burnt gas are shown in Table 1. Values of the flame speed relative to the unburnt gas are included in this table.

### Discussion

The systems studied here show the behaviour of  $H_2 + O_2$  mixtures burning with a second fuel ( $NH_3$ ), a second oxidant ( $N_2O$ ) or an inert diluent ( $N_2$ ). Measurements of flame speeds and composition limits of flammability in ternary mixtures reveal the effects of two combustion processes occurring simultaneously; in the present study the processes are the combustion of  $H_2$  and  $NH_3$  with  $O_2$ , and  $H_2$  with  $O_2$  and  $N_2O$ . Although, by themselves, these measurements do not permit a unique kinetic scheme to be established, they do provide a framework into which any detailed scheme must fit. For example, from the two expressions<sup>13, 14</sup>  $S_L^2 \propto P^{n-2}$  and  $S_L^2 \propto \exp(-E/RT_f)$ , showing the dependence of flame speed on total pressure and final flame temperature, values of the overall reaction order  $n$ , and activation energy  $E$ , can be estimated.

Before examining the systems in detail, three general observations can be made. First, in the combustion of ternary mixtures not far from stoichiometric, any excess of unstable reactant ( $NH_3$  or  $N_2O$ ) is decomposed into its elements. Measured pressure changes during combustion

support this conclusion. Secondly, flame temperatures for stoichiometric mixtures, with the exception of those diluted by nitrogen, vary by only 165°K (from 2790° to 2625°K). This temperature levelling effect, common in flames, is caused by dissociation of the burnt gas. Thirdly, since in flames, the bulk of the reaction occurs at temperatures near the final flame temperature (2600° to 2800°K) many of the elementary reactions occurring have rate constants (calculated from the best data<sup>1</sup> available for these temperatures), which vary only by a factor of up to 20. Thus the relative rates of these reactions depend largely on the concentrations of the reacting species.

### Comparison with previous work for binary systems

The chief binary system is  $H_2 + O_2$ . Previous determinations of composition limits of flammability for this system have been documented by Coward and Jones<sup>15</sup>. For upward propagation at 1 atm pressure, the extremes recorded are 3.9 and 95.8 per cent of hydrogen. In the present work, the limits occurred at 4.5 and 87.4 per cent of hydrogen at 70 mm, and 4.5 and 81.4 per cent of hydrogen at 50 mm of mercury. The normal narrowing of the range of flammability with decreasing pressure is observed. The lean limit is altered only slightly, but the rich limit much more markedly.

The flame speeds of near-stoichiometric  $H_2 + O_2$  mixtures are over 1000 cm sec<sup>-1</sup>, and it is these high values which cause experimental difficulties in the measurement of flame speeds. The high flow rates required to prevent flashback mean that with burner methods, very narrow tubes (diameter  $\leq 1$  mm) must be used to preserve laminar flow. Such small flames involve high curvature and render accurate measurements on the cone extremely difficult.

The previous values reported for the burning velocity ( $S_L$ ) in stoichiometric  $H_2 + O_2$  mixtures show considerable scatter. Most of the work refers to 1 atm pressure. Using burner methods, Senior<sup>16</sup> found 1120 cm sec<sup>-1</sup>, Bartholomé<sup>17</sup> obtained 1100 cm sec<sup>-1</sup> and Behrens<sup>18</sup> found 860 cm sec<sup>-1</sup>; by the constant-pressure bubble method, Strauss and Edse<sup>19</sup> obtained a value of 1400 cm sec<sup>-1</sup>; and Agnew

TABLE 1. Adiabatic flame temperatures, equilibrium burnt gas composition and flame speeds for combustion at 70 mm of mercury

System	Original composition, mole per cent			Flame speed, cm sec <sup>-1</sup>		Flame tem- perature °K	Final composition, mole per cent							
	H <sub>2</sub>	O <sub>2</sub>	X	S <sub>B</sub>	S <sub>V</sub>		H <sub>2</sub> O	H <sub>2</sub>	H	O <sub>2</sub>	O	OH	N <sub>2</sub>	NO
H <sub>2</sub> + O <sub>2</sub>	63	37	—	4180	602	2780	54.2	11.7	8.6	9.4	5.0	11.1	—	—
	66.7	33.3	—	4100	590	2790	54.4	15.5	10.2	5.8	4.1	10.0	—	—
	70.8	29.2	—	3960	569	2780	53.8	21.2	11.4	2.8	2.7	8.1	—	—
NH <sub>3</sub> + O <sub>2</sub> (X = NH <sub>3</sub> )	—	37.5	62.5	855	82	2160	49.6	16.1	5.1	0.9	0.8	3.7	23.1	0.3
	—	42.9	57.1	1200	120	2625	52.1	9.8	4.3	3.3	1.5	5.4	21.8	0.7
	—	46.4	53.6	1255	130	2630	52.8	6.6	3.3	6.6	2.2	6.2	20.9	0.9
H <sub>2</sub> + N <sub>2</sub> O (X = N <sub>2</sub> O)	20	—	80	855	89	2440	13.2	0.4	0.4	20.6	1.6	2.5	59.5	1.9
	50	—	50	3440	379	2710	30.2	8.5	6.0	2.9	2.3	5.1	44.1	0.8
H <sub>2</sub> + O <sub>2</sub> + NH <sub>3</sub> (X = NH <sub>3</sub> )	20	40	40	2200	239	2675	52.4	11.2	5.8	4.0	2.2	6.7	17.1	0.7
	42	37	21	3800	428	2730	52.8	13.1	7.6	4.7	2.9	8.1	10.2	0.5
	30	30	40	1500	165	2570	49.4	25.4	5.2	0.2	0.3	2.2	17.5	0.1
H <sub>2</sub> + O <sub>2</sub> + N <sub>2</sub> O (X = N <sub>2</sub> O)	55	10	35	4740	562	2725	37.0	10.1	6.4	3.5	2.4	6.2	33.5	0.9
	60	20	20	4650	596	2750	43.8	12.3	7.8	4.4	3.1	7.2	20.7	0.8
	65	30	5	4240	590	2775	52.2	14.5	9.1	5.3	3.6	9.5	5.6	0.5
H <sub>2</sub> + O <sub>2</sub> + N <sub>2</sub> (X = N <sub>2</sub> )	60	30	10	3550	517	2740	50.8	13.2	7.9	4.8	3.1	8.1	11.7	0.7
	50	25	25	2580	400	2650	44.7	9.6	4.9	3.3	1.8	5.5	29.4	0.8
	40	20	40	1700	262	2530	37.6	6.3	2.6	2.1	0.9	3.3	46.6	0.6

and Graiff<sup>20</sup> found  $1150 \text{ cm sec}^{-1}$  in a constant-volume spherical bomb. The most reasonable value for  $S_D$  at 1 atm appears to be *ca.*  $1120 \text{ cm sec}^{-1}$ . Our value for  $S_D$  at 70 mm of mercury is  $590 \text{ cm sec}^{-1}$ . Thus, the flame speed decreases with decreasing pressure over this pressure range, indicating an overall order of *ca.* 2.5.

In addition, the dependence of burning velocity on pressure has been studied<sup>19,20</sup> by Strauss and Edse\* from 1 to 100 atm, and by Agnew and Graiff<sup>20</sup> from 0.5 to 5 atm. In both cases, the burning velocity increases with pressure. Agnew and Graiff<sup>20</sup> report a logarithmic relation between flame speed and pressure, although the values for the burning velocity displayed on a small graph appear to differ from those obtained from the empirical expression they give. Their results when fitted to the relation  $S_D^2 \propto P^{n-2}$  lead to values for *n* of *ca.* 2.6 from the diagram, and *ca.* 2.15 from the empirical expression over their pressure range.

Additional support for the conclusion that *n* is greater than two comes from the pressure exponent of the burning velocity measured by Fine<sup>22</sup>. Measurements of burning velocity made by the constant-volume bomb technique yielded a reaction order *n* of 2.10, while a value for *n* of 2.38 was found from flame speeds of burner flames, obtained by measuring the total area of the Schlieren cone. Fine<sup>23</sup> has also measured the change with pressure and with flame temperature of the critical boundary velocity gradient for flashback, for sub-atmospheric flames of  $\text{H}_2 + \text{O}_2$  diluted with nitrogen or argon. From this, he deduced overall orders of *ca.* 2.3 with  $\text{N}_2$  as diluent, and *ca.* 2.15 with Ar as diluent.

The present measurements of flame speeds for  $\text{H}_2 + \text{O}_2 + \text{N}_2$  mixtures were made to provide a 'neutral' basis for assessing the behaviour of  $\text{H}_2 + \text{O}_2$  mixtures, to which either additional fuel or additional oxidant had been added. (It was not possible from the temperature dependence of flame speed to obtain a meaningful value for the effective overall activation energy.)

\* The work of Strauss and Edse<sup>19</sup> at high pressure has been criticized<sup>21</sup> as the flame front may become roughened, leading to increased flame speeds.

The burning velocities and flammability limits for the  $\text{NH}_3 + \text{O}_2$  and  $\text{H}_2 + \text{N}_2\text{O}$  systems have recently been measured by Andrews and Gray<sup>3</sup>, and by Armitage and Gray<sup>4</sup>, using the same apparatus and experimental conditions as in the present work. Both sets of measurements agree well with the present results. Comprehensive comparisons with earlier work have already been made<sup>3,4</sup> by Andrews and Gray for the  $\text{NH}_3 + \text{O}_2$  system, and by Armitage and Gray for  $\text{H}_2 + \text{N}_2\text{O}$ . For both systems, the values of  $S_D$  are effectively constant as the pressure changes. This indicates for each system an overall reaction order *n* of two.

#### *Behaviour of the ternary system $\text{H}_2 + \text{O}_2 + \text{NH}_3$ and its flame chemistry*

Little systematic work has been done on the composition limits of flammability and flame speeds for this system. Flammability limits for ternary mixtures at 1 atm pressure have been studied by Jorissen and Ongkiehong<sup>8</sup>, and for the special case  $2x \text{H}_2 + x \text{O}_2 + (1-x) \text{NH}_3$  at 0.5 atm by Partington and Prince<sup>9</sup>. The limits determined<sup>8</sup> by Jorissen and Ongkiehong effectively obeyed the Le Chatelier rule. In the present work, the lean limit lay wholly outside that determined by Jorissen and Ongkiehong and the rich limit lay partly outside theirs. However, as their measurements were made for downward propagation in a tube of 15 mm diameter, the apparent contrast between the two sets of results is not significant.

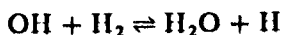
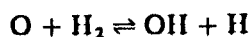
Some flame speeds in  $\text{H}_2 + \text{O}_2 + \text{NH}_3$  mixtures at atmospheric pressures have been reported by Ausloos and van Tiggelen<sup>6</sup>, and for the special case  $(1-x)(\text{NH}_3 + \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{N}_2) + x \text{O}_2$  by Murray and Hall<sup>7</sup>, who were interested in the stoichiometrically equivalent hydrazine + oxygen systems. For a mixture of composition 30 per cent  $\text{H}_2 + 30$  per cent  $\text{O}_2 + 40$  per cent  $\text{NH}_3$ , Ausloos and van Tiggelen obtained<sup>6</sup> a value for  $S_D = 157 \text{ cm sec}^{-1}$ . Our derived value for  $S_D$  at this composition is  $165 \text{ cm sec}^{-1}$ . It appears that in this region, flame speeds have no pressure dependence, again implying second order kinetics.

In our own work at 70 mm of mercury, the behaviour of the  $\text{H}_2 + \text{O}_2 + \text{NH}_3$  system shows a smooth transition between the two binary



systems. Calculated flame temperatures for stoichiometric mixtures decrease monotonically as  $\text{NH}_3$  replaces  $\text{H}_2$ , falling from 2790°K for stoichiometric  $\text{H}_2 + \text{O}_2$  to 2625°K for stoichiometric  $\text{NH}_3 + \text{O}_2$ . Flame speeds also decrease along the stoichiometric line from the  $\text{H}_2 + \text{O}_2$  extreme to the  $\text{NH}_3 + \text{O}_2$  extreme. The flammability region at low pressure is slightly broader than the Le Chatelier rule predicts, and flame speed contours are parallel to the limits. This behaviour would be in accord with simultaneous oxidations of  $\text{H}_2$  and  $\text{NH}_3$ , with little or no interaction between the two mechanisms. The temperature dependence of flame speeds for stoichiometric mixtures varies with the  $\text{H}_2/\text{NH}_3$  ratio, and no explanation is possible in terms of a single rate-controlling reaction. This behaviour is identical with that observed<sup>4</sup> for the combustion of hydrogen and ammonia supported by nitrous oxide.

At the  $\text{H}_2 + \text{O}_2$  extreme, the main reactions occurring<sup>1</sup> in the flame zone are:



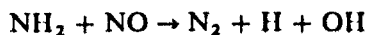
At the high temperatures of the flames, these reactions will rapidly become balanced, and all six species involved be in equilibrium.

The reactions occurring in  $\text{NH}_3 + \text{O}_2$  flames have been studied by Fenimore and Jones<sup>10</sup>, who concluded that all the molecular oxygen was consumed by the reaction\*



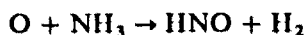
Nitric oxide was always found in the reaction zone, formed by the attack of oxygen atoms on ammonia (probably via the reactions  $\text{O} + \text{NH}_3 \rightarrow \text{HNO} + \text{H}_2$ ;  $\text{H} + \text{HNO} \rightarrow \text{H}_2 +$

$\text{NO}$ ). Thus the reaction



is also important in flames involving ammonia and oxygen.

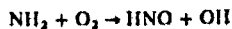
In a ternary mixture, the oxygen atoms probably react in three main ways:



As ammonia replaces hydrogen the last of these reactions becomes increasingly more important. Also with increasing  $\text{NH}_3$  concentration, flame temperatures are lowered and hence flame speeds decrease.

It is not yet possible for further knowledge of the reactions occurring in the flame to be gained from a knowledge of the isothermal reaction of hydrogen and ammonia with oxygen. Although the oxidation has been studied by Volders and van Tiggelen<sup>25</sup> and by Williamson and Pickles<sup>26</sup>, it is complicated and the detailed mechanism has not yet been elucidated. Volders and van Tiggelen, working between 380° and 430°C, found<sup>25</sup> that the addition of hydrogen to ammonia and oxygen greatly accelerated the reaction, without altering the activation energy. They also observed that the proportions of hydrogen and ammonia that were oxidized depended on their relative concentrations, but were independent of temperature. Williamson and Pickles studied<sup>26</sup> the effect of only small amounts of ammonia on the hydrogen-oxygen reaction. They found that the induction period before explosion was inversely proportional to the ammonia concentration, and postulated the formation of a sensitizer, the nature of which was unknown, although they eliminated nitric oxide and nitrogen dioxide as possible sensitizers.

\* A different scheme has been proposed by Husain and Norrish<sup>24</sup> to explain the flash photolysis of  $\text{NH}_3 + \text{O}_2$ . They postulated that the reaction



consumed molecular oxygen and led to the formation of nitric oxide. However, in their apparatus  $\text{NO}$  and  $\text{N}_2\text{O}$  were the nitrogenous products, whereas in flames  $\text{N}_2$  is the major product and there may be considerable differences between the two systems.

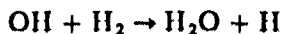
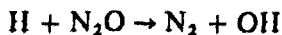
### *Behaviour of the ternary system $\text{H}_2 + \text{O}_2 + \text{N}_2\text{O}$ and its flame chemistry*

No previous results have been reported for flame speeds or flammability limits for  $\text{H}_2 + \text{O}_2 + \text{N}_2\text{O}$  mixtures, although Scott *et al.*<sup>27</sup> have determined the composition limits of flammability for  $\text{H}_2$  + air +  $\text{N}_2\text{O}$  mixtures.

The main interest in the present results lies in the departures of the rich flammability limits of the ternary system from the predictions of the *Le Chatelier* rule, and in the composition dependence of flame speed. Flame speeds ( $S_B$ ) increase as nitrous oxide replaces oxygen, reaching the maximum value at a composition 58 per cent  $H_2$  + 12 per cent  $O_2$  + 30 per cent  $N_2O$ , and then decrease as further oxygen is replaced. On the other hand, flame temperatures decrease monotonically from 2790°K for stoichiometric  $H_2$  +  $O_2$  to 2710°K for stoichiometric  $H_2$  +  $N_2O$  mixtures. The burning velocities ( $S_U$ ) relative to the unburnt gas follow a pattern similar to, but less marked than, that displayed by  $S_B$ . The values of  $S_U$  remain practically constant until *ca.* 25 per cent oxygen has been replaced by nitrous oxide, and then fall rapidly with increasing  $N_2O$  concentration. The considerable extent of the dissociation in these flames could account for the difference in behaviour shown by  $S_B$  and  $S_U$ .

This behaviour, which was certainly not displayed by the  $NH_3$  +  $O_2$  +  $N_2O$  system<sup>4</sup>, cannot be due to differences in the physical properties of oxygen and nitrous oxide, and is undoubtedly chemical in origin. From an analysis of the dependence of the flame speed on flame temperature, it is obvious that no explanation is possible in terms of a single rate-controlling step, operating over the whole system. It was found<sup>4</sup> for the  $NH_3$  +  $O_2$  +  $N_2O$  system also, that it was impossible to explain the flame speed contours in terms of a single rate-controlling step.

Although a satisfactory explanation of the behaviour of the  $H_2$  +  $O_2$  +  $N_2O$  system must be sought in terms of the detailed steps of a kinetic scheme, it is not possible at present to postulate these steps with any certainty. The elementary reactions for the  $H_2$  +  $O_2$  system have already been noted (see the section on the  $H_2$  +  $O_2$  +  $NH_3$  system). The binary  $H_2$  +  $N_2O$  system is well known from the slow oxidation work of Melville<sup>28</sup> and the flame studies by Fenimore and Jones<sup>11</sup>. The propagation steps are thought to be:



At first sight, it appears likely that the observed dependence of flame speed on composition can be explained by the presence of some intermediate, formed in a reaction between  $O_2$  and  $N_2O$ . Nitric oxide or nitrogen dioxide are the most likely intermediates. Nitric oxide is present in these flames, being formed via the reaction  $O + N_2O \rightarrow 2NO$ , and nitrogen dioxide could probably be formed by reactions of NO with  $N_2O$  (or  $O_2$ ). Moreover, our calculations show that the maximum flame speed occurs at a composition giving the highest value for the equilibrium concentration of nitric oxide in the burnt gas. Accordingly, to throw more light on the kinetic mechanism, flame speeds were determined in stoichiometric mixtures of  $H_2$  +  $O_2$  and  $H_2$  +  $O_2$  +  $N_2O$ , containing small amounts (up to one per cent) of nitric oxide. The flame speeds did not increase as nitric oxide was added. For an  $H_2$  +  $O_2$  mixture with one per cent of added nitric oxide, the flame speed was actually reduced (by about three per cent). The same result has also been obtained by Strauss and Edse<sup>19</sup>. Also Scott *et al.*<sup>27</sup> found that the composition limits of flammability at 1 atm for  $H_2$  + air + NO narrowed sharply with increasing NO concentration until 20 to 30 per cent NO had been added, when the limits widened again. In view of this evidence, it seems that NO and  $NO_2$  have an inhibiting effect on the reaction.

It is also interesting to note that for stoichiometric mixtures, the calculated equilibrium value for the H-atom concentration is a minimum at the composition for which the flame speed reaches its maximum value.

Synergistic behaviour, as displayed by the  $H_2$  +  $O_2$  +  $N_2O$  system, is uncommon in combustion. For the  $H_2$  + air +  $N_2O$  system, the rich and lean flammability limits, as reported by Scott *et al.*, effectively obeyed the *Le Chatelier*<sup>2</sup> rule in the normal way. Similarly, synergistic behaviour is not observed in the spontaneous ignition of  $H_2$  +  $O_2$  +  $N_2O$ . Danby and Hinshelwood<sup>29</sup> found that  $N_2O$  added to  $H_2$  +  $O_2$  mixtures acted as an inert diluent, although  $O_2$  added to mixtures of  $H_2$  +  $N_2O$  caused immediate explosion. This is obviously a one-sided effect, and quite different from the behaviour observed in  $H_2$  +  $O_2$  +  $N_2O$  flames. Also

Melville<sup>30</sup> found that  $N_2O$  inhibited the  $H_2 + O_2$  reaction, whereas  $O_2$  added to  $H_2 + N_2O$  mixtures greatly increased the rate of reaction.

Other examples of synergistic behaviour observed in flames are the  $N_2H_4 + N_2O + NO$  system, which has been studied by Gray, Mackinven and Smith<sup>31</sup> and the  $NH_3 + N_2O + NO$  system, studied by Armitage and Gray<sup>4</sup>. However, for this latter system, the behaviour was paralleled in the slow oxidation reaction, studied by Volders and van Tiggelen<sup>32</sup>, and in the spontaneous ignition. Thus, Poole and Graven<sup>33</sup> found that the addition of  $N_2O$  caused marked decreases in the ignition temperatures of  $NH_3 + NO$ , and Destriau and Laffitte<sup>34</sup> observed that the ignition of  $NH_3 + N_2O$  was aided by the addition of  $NO$ .

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