Combustion of Ammonia Supported by Oxygen, Nitrous Oxide or Nitric Oxide: Laminar Flame Propagation at Low Pressures in Binary Mixtures

D. G. R. ANDREWS and P. GRAY

Department of Physical Chemistry, University of Leeds, Leeds 2

Measurements of burning velocity in binary mixtures of ammonia with oxygen, nitrous oxide and nitric oxide have been made at sub-atmospheric pressures. Mixtures were ignited in a closed vessel and flame speeds (S_B) measured by schlieren photography with a drum camera. The stoichiometry of reaction and the effects upon the flame speed of (a) variation in the mixture composition over the whole range of flammability, (b) variation in the initial reactant pressure and (c) addition of inert diluents (helium, argon and nitrogen) have been investigated. Composition limits of flammability were also recorded.

In each system, combustion of a balanced mixture led to nitrogen and water, very little nitric oxide being found. In rich mixtures, the excess ammonia decomposed and in lean mixtures, the excess nitrous or nitric oxide. Maximum burning velocities occurred at or near stoichiometric proportions except in the nitric oxide system, where a rich mixture burned fastest. (Parallel behaviour was found in hydrazine flames.) Burning velocities were not significantly affected by total pressure, in concordance with an overall kinetic expression of the second order.

To obtain flame speeds relative to unburnt gases (S_U), the adiabatic flame temperatures and the equilibrium compositions of the hot products were calculated for mixtures corresponding to (i) complete combustion and (ii) maximum burning velocity. Flames supported by oxygen burned fastest; flames supported by nitric oxide were hottest but burned least rapidly. This order is in accord with the known relative reactivities in low temperature reactions and the same pattern of speeds was repeated in the order of diminishing resistance to quenching by inert diluents: $O_2 > N_2O > NO$ and in the width of the composition limits of flammability.

Introduction

ALTHOUGH well-defined experiments on the combustion of ammonia were carried out[1] by W. HENRY in Manchester 150 years ago, measurements of burning velocity have been made only in about the last decade. In 1951, R. C. MURRAY and A. R. HALL[2] reported the first values for the speeds of oxygen–ammonia flames, and in the same year P. AUSLOOS and A. VAN TIGGELEN[3] measured the speeds of both oxygen–ammonia and nitrous oxide–ammonia flames; in 1953 W. G. PARKER and H. G. WOLFHARD[4] reported burning velocities in nitrous oxide–ammonia and nitric oxide–ammonia mixtures. (Subsequent work is referred to later.)

The present work on flame speeds in ammonia combustion supported by oxygen, nitrous oxide or nitric oxide was undertaken for three reasons. First, to extend the existing results at atmospheric pressure to low pressures and, to improve the precision—speeds in some experiments are quoted to ± 30 per cent; secondly, to enable comparisons to be made between hydrazine (with which our previous work[5, 6] has been concerned) and ammonia as fuels and between oxygen, nitrous oxide and nitric oxide as oxidants; and thirdly, to throw light on the possible formation and combustion of ammonia in hydrazine flames. A subsequent paper[7] describes the results of laminar flame speed

measurements in ternary mixtures of these substances.

In the previous work, closed-vessel measurements were made[5,6]—partly for their greater convenience (they consume smaller amounts of hazardous monofuels such as hydrazine and dimethyl hydrazine)—but mainly because they permitted better control of conditions (initial pressure and temperature) and avoided difficulties of accurately metering vaporized liquid fuels. Not all these difficulties apply to ammonia combustion, but closed vessel measurements have been again adopted in order to make comparisons under identical conditions. The technique has the added advantage that curvature of the flame is considerably less here than in burner experiments.

The present experiments are principally concerned with measurements of laminar flame speeds, though the composition-limits of flammability at low pressures (70 mm of mercury) have also been measured. The dependence of flame speed on ammonia/oxidant ratio, the location and speed of the fastest flames, the influence on flame speed of added inert diluents (helium, argon and nitrogen) and of varying initial pressure have all been examined. In addition, calculations have been made of the adiabatic flame temperatures and of the composition of the hot, burnt gases. Values of these properties are necessary to convert the experimentally measured speeds into velocities relative to the unburnt gas S_U (e.g. for comparison with results of other workers). They are also important in the comparison of systems (NH_3 and N_2H_4; O_2, N_2O and NO), in the interpretation of velocity/composition diagrams for ternary mixtures[7] and in the theory of flames.

Experimental

Materials
Ammonia, oxygen and nitrous oxide (medical grade) were taken from cylinders. Nitric oxide was prepared[8] by reducing aqueous sodium nitrite with ferrous sulphate dissolved in dilute sulphuric acid. After removal of acid spray, nitrogen dioxide and water, it was freed from traces of nitrous oxide and nitrogen by fractionation *in vacuo*.

Helium, argon and nitrogen, which were used as inert diluents, were also taken from cylinders.

Apparatus
Combustion vessel and thermostat—The combustion vessel was a flanged glass cylinder (20 cm i.d., 20 cm long) closed by circular plate-glass windows sealed to the flanges with black wax. Tungsten electrodes (1 mm diameter) with rounded tips projected horizontally from opposite sides of the vessel to form a spark gap 4·6 mm long. The vessel was connected by a conventional vacuum line to manometers and to storage bulbs for liquids and gases; the whole system could be evacuated by a two-stage rotary pump.

To prevent condensation, the manometers and vacuum line were heated electrically and the combustion vessel was enclosed by an air thermostat. The temperature inside the vessel was uniform to within 2°C.

Optical system—The movement of the flame was followed on a rotating drum camera by a schlieren technique[9]: a detailed account of the apparatus is given by J. C. LEE[10]. The light-source was a Phillips 500 W mercury-vapour lamp, and a large concave mirror (diameter, 20 cm; radius of curvature, 183 cm) was used to send the light twice through the flame. The field of view was restricted to a narrow section of the flame along the vertical diameter, and the progress of the flame in this direction was recorded (as a V-shaped trace) on a film moving horizontally in a rotating-drum camera made by Southern Instruments Ltd (Model M 731). The speed of the drum was found by timing a spindle driven through a 300/1 reduction gear. The optical magnification (of the spark gap) was 0·228. Panchromatic 35 mm film (Kodak R 60 or Ilford R 101) was used.

Procedure
Gaseous mixtures were prepared and allowed to mix in the combustion vessel. To check that mixing was complete, duplicate experiments were done on mixtures made up in a different order. Initial and final pressures were measured

as routine, and chemical analysis of reaction products made in representative cases.

Composition-limits of flammability—For the purposes of internal comparison between oxygen, nitrous oxide and nitric oxide, composition-limits of flame propagation were measured in the combustion vessel under the same conditions as the flame-speed measurements (pressure 70 mm of mercury; temperature 60°C).

Flame-speed measurements—A mixture was prepared in the combustion vessel and the camera was run at a suitable, uniform speed.

Opening the shutter of the camera triggered the spark which in turn ignited the gaseous mixture. To minimize any influence of the spark on propagation, a range of condensers of different capacities was available so that the spark-energy used was never grossly in excess of the minimum necessary for ignition. The speed of the drum was measured immediately before and after ignition.

The photographic record showed that, usually after a short initial period of acceleration, the movement of the flame was uniform until it reached a diameter of 9–10 cm ($r_B \simeq 0.5\,R$). The traces were enlarged and tangents drawn at the point corresponding to a flame diameter of 6 cm, i.e. 30 per cent of the vessel diameter. There was no significant difference between the slopes of the upper and lower traces, showing that any convective lifting of the flame sphere was negligible. The mean slope was used to calculate the flame speed, yielding a probable error of about two per cent in the most favourable cases and of about five per cent in acceleratory reactions (where it is harder to draw tangents accurately). All flame speeds reported are the average of at least two determinations.

Interpretation of the traces—After a gas is ignited at the centre of a closed vessel[11,12] and the flame begins to travel towards the walls, the pressure rises and both the burnt and unburnt gases are compressed. As a result, the movement of the flame depends on the gas flow as well as on the burning rate. However, during the initial phase of the combustion the increase in pressure is small and the linear speed of the flame (S) is very nearly equal to the speed of the flame relative to the burnt gas (S_B). Even when the radius of the flame sphere r_B is $0.3\,R$ (where R is the radius of the vessel) the pressure has risen by only three per cent and the speed S differs from S_B by only two per cent. The speed of the flame measured at this point is therefore essentially the speed relative to the burnt gas at the initial pressure.

For the evaluation of the speed of the flame relative to the unburnt gas (S_U) it is necessary to know the *expansion ratio* (V_B/V_U) which depends both on the numbers of molecules produced by combustion and on the flame temperature. In stoichiometric mixtures, combustion of the ammonia is complete and a reliable value for S_U may readily be calculated by assuming equilibrium conditions in the hot gases. Far from stoichiometric proportions, non-equilibrium conditions do not permit such calculations to be made with confidence.

Calculations of flame temperature and burnt-gas composition—Thermodynamic properties from standard compilations[12,13] were used in the calculation[14] of final flame temperatures and burnt gas composition.

Results
### (a) Oxygen–Ammonia Flames

Under the conditions of these experiments (initial pressure 70 mm of mercury and temperature 60°C) flames could be propagated in mixtures containing between 23 and 61·5 per cent ammonia.

In the stoichiometric mixture (57·1 per cent NH_3), the pressure increase after explosion approximated closely to that for complete oxidation (equation 1) and no nitric oxide was detected (either chemically or when the gaseous products were analysed in the mass spectrometer).
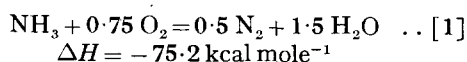
$$NH_3 + 0.75\,O_2 = 0.5\,N_2 + 1.5\,H_2O \quad .. [1]$$
$$\Delta H = -75.2\,\text{kcal mole}^{-1}$$

The pressure increase after explosion was meas-

ured over the whole range of composition and is recorded in *Figure 1*. In somewhat lean mix-
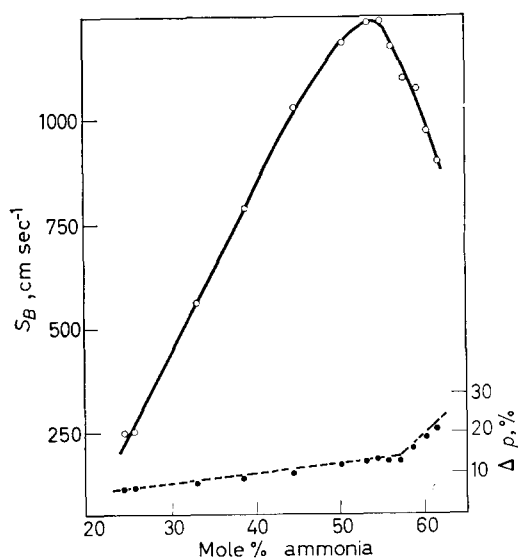
Figure 1. Oxygen–ammonia mixtures. Dependence of burning velocity (S_B, cm sec^{-1}) on composition (mole per cent NH₃). Total pressure, 70 mm Hg; initial temperature, 60°C. Solid line ——— burning velocity; broken line - - - - - calculated percentage pressure increase, ● observed pressure increase

tures, all the ammonia was oxidized and the excess oxygen survived unchanged. However, in rich mixtures, the pressure increase indicated that while the stoichiometric proportion of ammonia was oxidized, the excess decomposed to nitrogen and hydrogen. The final products must now be represented by a combination of equations 1 and 2.

$$NH_3 = 0.5\,N_2 + 1.5\,H_2 \qquad \dots\,|\,2\,]$$
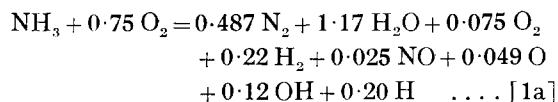$$\Delta H = -11.04\,\text{kcal mole}^{-1}$$
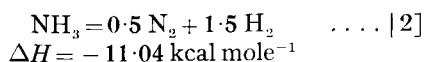
The broken line in *Figure 1* represents the percentage pressure increase after combustion predicted on this basis and the points on it are the pressure increases actually observed. The expectations are borne out over the range of composition studied, though it must be recognized that in lean mixtures some nitric oxide could be formed, since its presence would not be revealed by pressure measurements.

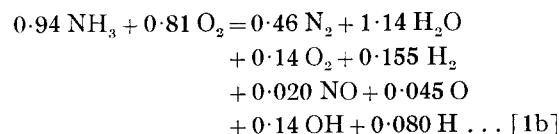## Laminar flame speeds: effect of composition

Flame speeds were measured over almost the whole range of flammability at 60°C and 70 mm of mercury total pressure. The results of these measurements are displayed in *Figure 1*. They show that the flame speed S_B had its maximum value of 1 250 cm sec^{-1} in a lean mixture (53 per cent ammonia); the velocity for the stoichiometric composition (57 per cent NH₃) is 1 100 cm sec^{-1}. The slowest flame measured, with a speed of *ca.* 250 cm sec^{-1} occurred in a lean mixture (24.3 per cent NH₃): on the ammonia-rich side the slowest flame speed was *ca.* 900 cm sec^{-1} in a mixture containing 61.4 per cent NH₃. However, in rich mixtures the initial acceleratory period was prolonged and accurate estimation of the burning velocity—especially near the rich limit—was more difficult.

For the stoichiometric mixture, though the final products are represented by equation 1, the equilibrium composition of the burnt gases before cooling is given by equation 1a.

$$NH_3 + 0.75\,O_2 = 0.487\,N_2 + 1.17\,H_2O + 0.075\,O_2$$
$$+ 0.22\,H_2 + 0.025\,NO + 0.049\,O$$
$$+ 0.12\,OH + 0.20\,H \qquad \dots\,[\,1a\,]$$

To this stoichiometry corresponds a final flame temperature of 2 350°C (2 625° ±5°K) and a flame speed relative to the unburnt gas (S_U) of 110 cm sec^{-1}.

For the mixture corresponding to the maximum value of S_B the equilibrium composition of the burnt gases before cooling is given by equation 1b:

$$0.94\,NH_3 + 0.81\,O_2 = 0.46\,N_2 + 1.14\,H_2O$$
$$+ 0.14\,O_2 + 0.155\,H_2$$
$$+ 0.020\,NO + 0.045\,O$$
$$+ 0.14\,OH + 0.080\,H \dots\,[\,1b\,]$$

The corresponding adiabatic flame temperature is 2 345°C (2 630° ±5°K) and the flame speed S_U is 127 cm sec^{-1}.

Effect of initial pressure on flame speed

In the stoichiometric mixture (NH₃ + 0.75 O₂) flames could not be ignited at total pressures

below 63 mm of mercury and velocity measurements were made only at that pressure and at 70 mm. The values found (1 200 cm sec^{-1} and 1 240 $\pm$ 10 cm sec^{-1}) do not reveal any significant dependence on pressure.

Effect of diluents on flame speed

The effect of diluents on flame speeds was investigated by making varying additions of diluent to a constant partial pressure (70 mm of mercury) of a stoichiometric ammonia–oxygen mixture. The results are summarized in *Table 1*. The diluents used were helium, argon and nitrogen.

an effect but more than 60 mm could not be added safely: ignition of one mixture of these proportions destroyed the reaction vessel.

(b) Nitrous Oxide–Ammonia Flames

Flames in nitrous oxide–ammonia mixtures could be propagated at 70 mm of mercury and 60°C in the combustion apparatus over a composition range from 17 to 44·5 per cent ammonia.

In the stoichiometric mixture (40 per cent NH_3) the pressure increase after explosion approximated closely to that for complete combustion (equation 3). Nitric oxide was not de-

Table 1. Influence of inert diluents (He, Ar, N_2) on ignitability and flame speed in low pressure ammonia flames. All entries refer to S_B in cm sec^{-1}: initial temperature 59·7°; partial pressure of diluent x mm Hg

System	x (mm Hg)	5	10	20	25	30	35	40	50	60
Oxygen–ammonia mixtures $P_{O_2} = 30$ mm $P_{NH_3} = 40$ mm S_B (undiluted) 1 100 cm sec^{-1}	*Helium*	—	1004	782	No ignition possible $x \geqslant 25$					
	Argon	—	993	788	—	679	—	546	—	*
	Nitrogen	—	903	659	—	517	—	386	—	—
Nitrous oxide–ammonia mixtures $P_{N_2O} = 43$ mm $P_{NH_3} = 27$ mm S_B (undiluted) 915 cm sec^{-1}	*Helium*	854	No ignition possible $x \geqslant 10$							
	Argon	—	729	616	—	487	—	410		
	Nitrogen		687	481	—	359	No flame possible $x \geqslant 35$			
Nitric oxide–ammonia mixtures $P_{NO} = 40$ mm $P_{NH_3} = 30$ mm S_B (undiluted) 530 cm sec^{-1}	*Helium*	No ignition possible for $x \geqslant 5$								
	Argon	—	526	420	—	348	—	252		
	Nitrogen	—	464	329	263	No flame possible $x \geqslant 30$				

*Flame propagated even when $x=60$, but vessel destroyed by explosion.

The diluents all diminished the flame speed. The order of increasing effectiveness was He < Ar < N_2. Helium actually quenched the system quite effectively, ignition being impossible when the partial pressure of helium was 25 mm of mercury. As those flame speeds which could be measured were not so very much lowered by helium this was ascribed to an influence on ignition rather than on propagation. In agreement with this, the acceleratory portion of the photographic record was prolonged by additions of helium. Argon did not show such

tected chemically, though traces were found in a mass-spectrometric analysis:
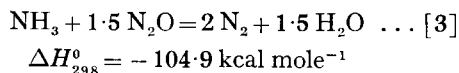
$$NH_3 + 1 \cdot 5\, N_2O = 2\, N_2 + 1 \cdot 5\, H_2O \;\ldots [3]$$
$$\Delta H^0_{298} = -104 \cdot 9 \text{ kcal mole}^{-1}$$

The pressure increase after explosion was measured over the whole range of composition and is recorded in *Figure 2*. In lean mixtures all the ammonia was oxidized; the excess nitrous oxide did not survive but decomposed to nitrogen and oxygen, so that the stoichiometry of
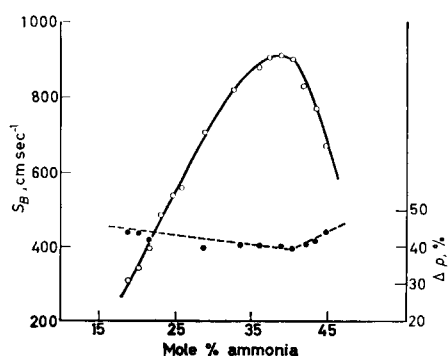
Figure 2. Nitrous oxide–ammonia mixtures. Dependence of burning velocity (S_B, cm sec^{-1}) on composition (mole per cent NH_3). Total pressure, 70 mm Hg; initial temperature, 60°C. Solid line —————— burning velocity; broken line - - - - - calculated percentage pressure increase, ● observed pressure increase

combustion in lean mixtures is to be represented by a combination of equations 3 and 4:

$$N_2O = N_2 + 0.5\,O_2 \qquad \ldots [4]$$
$$\Delta H_{298}^0 = -19.6\ \text{kcal mole}^{-1}$$
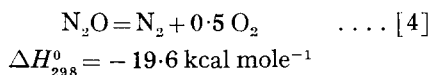
In ammonia-rich mixtures, as before, excess ammonia underwent decomposition to nitrogen and hydrogen (see equation 2 above). The broken line in *Figure 2* represents the percentage pressure increase in combustion predicted on the basis of equations 2, 3 and 4: the points on it are the observed pressure increases. The expectations are substantially borne out over the composition range studied.
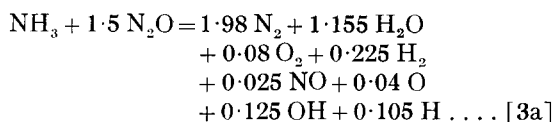
Laminar flame speeds: effect of composition
Flame speeds were measured over almost the whole range of ignitability; *Figure 2* displays the results. The flame speed S_B in the stoichiometric mixture (40 per cent NH_3) is 908 cm sec^{-1}; the maximum value (915 cm sec^{-1}) is very slightly to the lean side (38 per cent NH_3) of stoichiometric proportions. The slowest flame speed measured was 310 cm sec^{-1} in a mixture containing 18·6 per cent NH_3.

In lean mixtures (less than 35 per cent ammonia) the photographic records were rectilinear from the point of initiation. An initial acceleration became perceptible as the percentage of ammonia increased, becoming very marked by the rich limit (44·3 per cent NH_3)

so that there the flame was still accelerating slightly even when $r_B = 0.3\,R$.

The equilibrium composition of the burnt gases before cooling was calculated for several initial compositions and pressures. For the stoichiometric mixture initially at 70 mm of mercury, the equation 3a represents the reaction.

$$NH_3 + 1.5\,N_2O = 1.98\,N_2 + 1.155\,H_2O$$
$$+\ 0.08\,O_2 + 0.225\,H_2$$
$$+\ 0.025\,NO + 0.04\,O$$
$$+\ 0.125\,OH + 0.105\,H\ \ldots\ [3a]$$

To this stoichiometry corresponds a final flame temperature of 2 310°C (2 580° ±5°K) and a flame speed relative to the unburnt gas of 78·4 cm sec^{-1}. The corresponding value of S_U for the mixture (38·57 per cent ammonia), in which the value of S_B was greatest, was 79 cm sec^{-1}.

Effect of initial pressure on flame speed
Flame speeds were measured in a series of stoichiometric mixtures at pressures from 70 to 49 mm of mercury. Below this pressure, the mixture was not ignitable. The annexed results show that S_B depends only slightly on pressure:

| Total pressure (mm Hg)	70	63	56	49	42
Burning velocity (cm sec^{-1})	908	894	899	874	no flame

Effect of diluents on flame speeds
The effect of inert diluents on flame speed was investigated by adding varying amounts of helium, argon or nitrogen to a constant amount (70 mm) of the 38·6 per cent NH_3 (maximum velocity) mixture. The results are summarized in *Table 1*.

All three diluents diminished the flame speed, nitrogen being more effective than argon, and helium showing a strong quenching effect on the ignition process.

(c) Nitric Oxide–Ammonia Flames
At 60°C with all mixtures initially at a total pressure of 70 mm of mercury, flames could be propagated in the ammonia–nitric oxide system over the range 27 to 53 per cent ammonia.

The pressure increase after explosion was measured over the whole range of composition (recorded in *Figure 3*) and some product analyses performed. In the stoichiometric mixture (40 per cent NH$_3$), combustion appeared to be complete (equation 5):

$$NH_3 + 1 \cdot 5\,NO = 1 \cdot 25\,N_2 + 1 \cdot 5\,H_2O \ .. \ [5]$$
$$\Delta H_{298} = -108 \cdot 1 \ kcal\,mole^{-1}$$
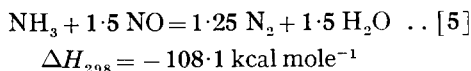
In rich mixtures, the excess of ammonia underwent decomposition and the stoichiometry of combustion in such mixtures has to be represented by a combination of equations 5 and 2. In lean mixtures, pressure measurements will not reveal whether the excess nitric oxide survived. A lean mixture containing 33 per cent NH$_3$ was exploded and the products withdrawn and examined. Mass spectrometric analysis revealed the presence of traces of a constituent of mass number 30. Chemical investigation, however, showed no sign of nitric oxide though as soon as a little nitric oxide was added to the products, nitrogen dioxide was observed: only oxygen was present in chemically significant amounts. The stoichiometry of combustion in lean mixtures may be represented by a combination of equations 5 and 6:

$$NO = 0 \cdot 5\,N_2 + 0 \cdot 5\,O_2 \qquad .... \ [6]$$
$$\Delta H = -21 \cdot 6 \ kcal\,mole^{-1}$$
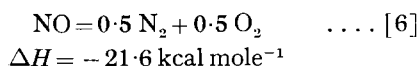
There are again two distinct ranges of product composition: rich mixtures in which all the oxidant is reduced to nitrogen and water and the excess ammonia is decomposed to nitrogen and hydrogen and lean mixtures in which all the ammonia is oxidized and the excess nitric oxide is decomposed to nitrogen and oxygen. Expectation and experiment are compared in *Figure 3*.

Laminar flame speeds: effect of composition

The flame speed (S_B) varied from 415 cm sec^{-1} near the lean limit through a maximum value of 700 cm sec^{-1} in a rich mixture (45 per cent NH$_3$) to 530 cm sec^{-1} near the rich limit (53 per

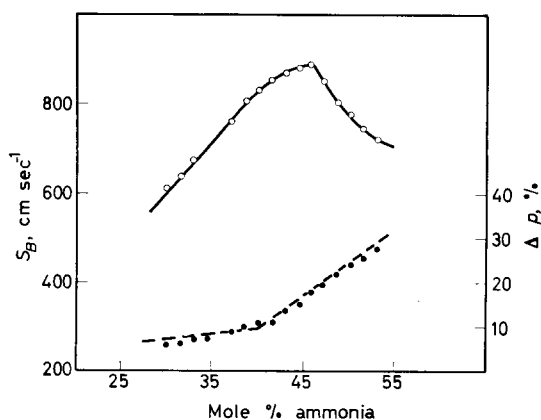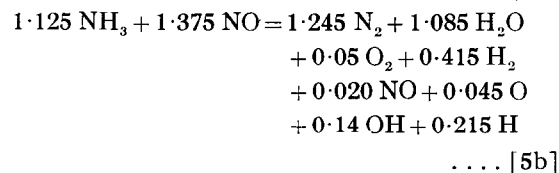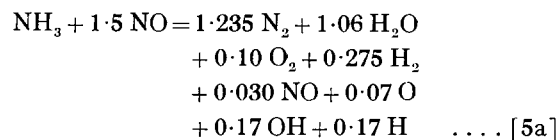*Figure 3. Nitric oxide–ammonia mixtures. Dependence of burning velocity (S_B, cm sec^{-1}) on composition (mole per cent NH$_3$). Total pressure, 70 mm Hg, initial temperature, 60°C. Solid line ——— burning velocity; broken line - - - - - calculated percentage pressure increase, ● observed pressure increase*

cent NH$_3$): all the flame speeds refer to mixtures initially at 70 mm pressure and 60°C. The results are displayed in *Figure 3*. In the stoichiometric mixture S_B was 640 cm sec^{-1}.

The photographic records revealed a brief initial acceleratory period which did not, however, become pronounced until ammonia-rich mixtures were reached.

The adiabatic constant-pressure flame temperature and the equilibrium composition of the burnt gases have been calculated for the stoichiometric mixture (equation 5a) and for the mixture giving the maximum flame speed (equation 5b).

$$NH_3 + 1 \cdot 5\,NO = 1 \cdot 235\,N_2 + 1 \cdot 06\,H_2O$$
$$+ 0 \cdot 10\,O_2 + 0 \cdot 275\,H_2$$
$$+ 0 \cdot 030\,NO + 0 \cdot 07\,O$$
$$+ 0 \cdot 17\,OH + 0 \cdot 17\,H \qquad .... \ [5a]$$
$$1 \cdot 125\,NH_3 + 1 \cdot 375\,NO = 1 \cdot 245\,N_2 + 1 \cdot 085\,H_2O$$
$$+ 0 \cdot 05\,O_2 + 0 \cdot 415\,H_2$$
$$+ 0 \cdot 020\,NO + 0 \cdot 045\,O$$
$$+ 0 \cdot 14\,OH + 0 \cdot 215\,H$$
$$.... \ [5b]$$

In the stoichiometric mixture (5a) the adiabatic flame temperature is 2 440°C (2 710° ±5°K)

and the flame speed relative to the unburnt gas 62·6 cm sec^{-1}; in the other mixture (5b) the corresponding values are $T_B = 2430°$C ($2700° \pm 5°$K) and $S_U = 65·5$ cm sec^{-1}.

Effect of initial pressure on flame speed
Flame speeds (S_B) were measured for mixtures of composition corresponding to the maximum burning velocity (45 per cent NH$_3$) at different initial pressures (P). Below 50 mm the mixture was not ignitable and over the accessible pressure range the variation of S_B with P was slight:

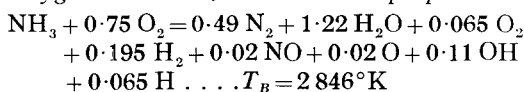| Total pressure (mm Hg)	70	63	56	49
Burning velocity (cm sec^{-1})	689	671	660	no flame

Effect of inert diluents on flame speed
To a constant amount (70 mm) of an ammonia–nitric oxide mixture of maximum burning velocity varying additions (x mm) of helium, argon or nitrogen were made. All the diluents lowered the flame speed, nitrogen being most effective. Dilution also prolonged the initial acceleratory period. Helium prevented ignition even when only 5 mm was added. *Table 1* summarizes the results.

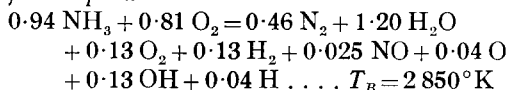### (d) Flame Temperatures and Burnt Gas Compositions in Ammonia Combustion at Atmospheric Pressure

To convert the present values of measured flame speeds to speed relative to unburnt gases, adiabatic flame temperatures and equilibrium product compositions had to be calculated for a constant-pressure flame at 70 mm of mercury. It is convenient to be able to make the same conversion for flames at 1 atm and the corresponding calculations have been performed. They are summarized below as chemical equations. For oxygen–ammonia flames, the results are in accord with the (small) diagram given[13] by A. G. GAYDON and H. G. WOLFHARD.

Oxygen–ammonia, stoichiometric proportions
NH$_3$ + 0·75 O$_2$ = 0·49 N$_2$ + 1·22 H$_2$O + 0·065 O$_2$
  + 0·195 H$_2$ + 0·02 NO + 0·02 O + 0·11 OH
  + 0·065 H . . . .$T_B = 2846°$K

The measured[15] value (sodium line reversal) of T_B is $2690°$K.

Oxygen–ammonia, mixture giving maximum flame speed
0·94 NH$_3$ + 0·81 O$_2$ = 0·46 N$_2$ + 1·20 H$_2$O
  + 0·13 O$_2$ + 0·13 H$_2$ + 0·025 NO + 0·04 O
  + 0·13 OH + 0·04 H . . . . $T_B = 2850°$K

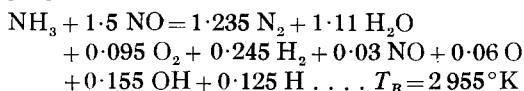The measured[15] value (sodium line reversal) of T_B is $2710°$K.

Nitrous oxide–ammonia
The stoichiometry and flame temperatures differ very little for the balanced mixture and for the mixture giving maximum flame speed. The stoichiometric mixture may be represented by the equation:
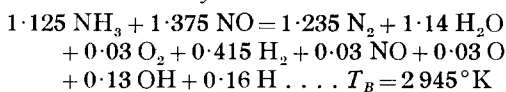
NH$_3$ + 1·5 N$_2$O = 1·98 N$_2$ + 1·21 H$_2$O + 0·075 O$_2$
  + 0·185 H$_2$ + 0·035 NO + 0·035 O
  + 0·11 OH + 0·075 H . . . . $T_B = 2780°$K
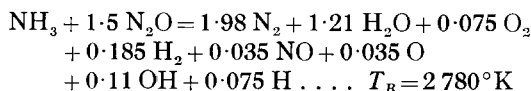
The measured[16] value of $T_{max.}$ is $2620°$K in a mixture containing 58·5 per cent N$_2$O.

Nitric oxide–ammonia, stoichiometric proportions
NH$_3$ + 1·5 NO = 1·235 N$_2$ + 1·11 H$_2$O
  + 0·095 O$_2$ + 0·245 H$_2$ + 0·03 NO + 0·06 O
  + 0·155 OH + 0·125 H . . . . $T_B = 2955°$K

H. G. WOLFHARD and W. G. PARKER calculated[17] a value of $2950°$K for T_B; their measured value was $2815°$K; G. K. ADAMS and G. W. STOCKS calculated[18] that $T_{max.}$ was reached in a lean mixture.

Nitric oxide–ammonia, mixture giving maximum velocity
1·125 NH$_3$ + 1·375 NO = 1·235 N$_2$ + 1·14 H$_2$O
  + 0·03 O$_2$ + 0·415 H$_2$ + 0·03 NO + 0·03 O
  + 0·13 OH + 0·16 H . . . . $T_B = 2945°$K

Discussion
Before making comparisons with previous measurements on ammonia combustion and discussing the contrasts between (i) oxygen,

nitrous oxide and nitric oxide as oxidants and (ii) hydrazine and ammonia as fuels, it is instructive to survey some of the general features. Perhaps the most notable is the 'levelling-down' of flame temperatures to values (at 70 mm of mercury) always within about 70° of 2 650°K. This arises from the molecular dissociation in the burnt products; this is more extensive the lower the pressure and more influential in determining T_B than either the exothermicity of combustion or the mole numbers of final products (which show 50 and 75 per cent variations per mole of ammonia burnt respectively). *Table 2* lists values for ΔH, T_B, S_B and S_U.

The relative abundance of the unstable species in the burnt gases also shows a consistent pattern. At the stoichiometric composition, H_2 is predominant, followed by HO, H and O_2 in similar amounts; O and NO are least abundant. In rich mixtures, H_2 is still more abundant, H overtakes HO, and O_2 takes a low place. In increasingly lean mixtures, O_2 moves up to first place, HO and O overlap H and H_2 while NO remains generally last.

The qualitative analyses of stable products made here are confined to regions fairly near to stoichiometric. They show that even in lean mixtures rather little nitric oxide is formed from the oxygen and nitrous oxide flames, and that little nitric oxide survives from the nitric oxide flames. Farther from stoichiometric proportions this may not remain true, but there seem to be real differences between these results at low pressures and those of others nearer 1 atm (W. G. PARKER and H. G. WOLFHARD[4, 17], e.g., implying that most excess nitric oxide survives, though that conclusion was based on qualitative spectroscopic evidence rather than analysis).

Inert diluents reveal only two of their three common influences. By reducing flame temperatures, diluents invariably reduce flame speeds: in all cases this effect is found. They may also exert a differential influence through their different thermal conductivities—helium giving rise to faster flames than argon on this account[5, 10, 13]. This effect is not found because it is overlaid by a third influence—that on ignition, all mixtures diluted with helium proving less easy to ignite than corresponding ones with argon, so that results for adequate ranges of helium-diluted mixtures could not be obtained.

Comparison with Previous Work

Two factors must be taken into account in making comparisons with existing measure-

Table 2. *Exothermicities, flame speeds and flame temperatures in ammonia combustion*

System and composition (P_U=70 mm; T_U=59·7°C)	$-\Delta H^0_{298}$ (kcal per mole NH_3)	T_B (°K)	S_B (cm sec⁻¹)	S_U (cm sec⁻¹)
Oxygen and ammonia				
(a) stoichiometric (57·1 per cent NH_3)	75·16	2 625	1 110	110
(b) max. velocity (53·6 per cent NH_3)	—	2 630	1 255	127
Nitrous oxide and ammonia				
(a) stoichiometric (40 per cent NH_3)	104·9	2 580	910	78
(b) max. velocity (38·6 per cent NH_3)	—	2 580	915	79
Nitric oxide and ammonia				
(a) stoichiometric (40 per cent NH_3)	108·1	2 710	635	62·5
(b) max. velocity (45 per cent NH_3)	—	2 700	690	65·5

ments. First, most previous measurements afford values of ammonia flame speeds relative to unburnt gas. The preceding section presents the data (flame temperatures and burnt gas compositions) necessary to convert either these S_U to S_B at 1 atm or our own S_B to S_U at 70 mm of mercury: we have generally chosen the latter alternative (though for hydrazine flames conversion is unnecessary). Secondly, while wholly valid for internal comparison, the composition limits for flame propagation reported here refer not to upward propagation in a tube but to central ignition in a large sphere. The effects observed are generally large enough for the geometry to be of secondary importance, however.

Oxygen–ammonia flames
Numerous measurements of flammability limits of oxygen–ammonia (and air–ammonia) mixtures have been made: the most complete appear to be those of A. G. WHITE[21]. He found (5 cm tube, 18°C) that the composition limits at 1 atm were:

Direction of propagation	*Upwards*	*Horizontal*	*Downwards*
Lean and rich limits (per cent NH$_3$)	15·3 to 79	16·7 to 79	18·1 to 79

J. R. PARTINGTON and A. J. PRINCE's measurements[1] made at 0·5 atm (85°C, 100 cm^3 bulb) led to a lean limit of *ca.* 21 per cent NH$_3$ and a rich limit *ca.* 74 per cent NH$_3$. Our own values (60°C) at 70 mm of 23 and 61 per cent show the influence of lowered pressure in narrowing the flammability range.

Flames burn fastest at these low pressures in somewhat lean mixtures (53·6 instead of 57·1 per cent NH$_3$). The same result was generally found at atmospheric pressure, maximum speeds having been reported for mixtures with ammonia percentages of 54·5[2] (for $T_U = 150°$), 57[2] (for $T_U = 25°$C), 53·5[3], 50[22] and 50·5[23]. Flame temperatures[13,15] also show maxima on the lean side. These locations of $S_{max.}$ and $T_{max.}$ have been variously attributed to the need for surplus oxygen to allow for the formation of

some nitric oxide[15] and to the fact[13] that ammonia is an exothermic compound.

The values reported for $S_U^{max.}$ in cm sec^{-1} at 1 atm are rather scattered. R. C. MURRAY and A. R. HALL[2] found 127 (for $T_U = 25°$C) and 170 (for $T_U = 150°$C) corresponding to 137 at $T_U = 60°$C. P. AUSLOOS and A. VAN TIGGELEN[3] found $S_U^{max.}$ 113 cm sec^{-1}; J. VAN WONTERGHEM and A. VAN TIGGELEN[15] found $S_U^{max.}$ was 145 cm sec^{-1}. L. COHEN[20] gave to $S_U^{max.}$ the value 150 cm sec^{-1}. In view of this scatter, the values at 1 atm and the value of 125 cm sec^{-1} found here at 70 mm of mercury are not significantly different, and from this and from our own measurements we conclude that flame speed does not depend significantly on pressure. Since theory[10,12,13] predicts $S \propto P^{(n-2)/2}$, the effective overall reaction order n is 2.

It is not easy to make comparisons with isothermal reaction kinetics, since the low-temperature oxidation of ammonia is extremely complex. J. VERWIMP and A. VAN TIGGELEN[21] in measurements made near 525°C found an overall activation energy *ca.* 50 kcal mole^{-1}; E. R. STEPHENS and R. N. PEASE[22] earlier reported a value *ca.* 45 kcal mole^{-1}. Activation energies derived[15] from measurements of flame speeds in diluted mixures are *ca.* 59 kcal mole^{-1}.

Nitrous oxide–ammonia flames
The only previous work on flammability limits of nitrous oxide–ammonia mixtures seems to be that of J. C. KERR and E. JONES[23]. At 1 atm and room temperature their reported values are:

Direction of propagation	*Upwards*	*Horizontal*	*Downward*
Lean and rich limits (per cent NH$_3$)	2·6 to 71·9	5·1 to 71·6	6·8 to 71·0

The lean limit for upward propagation is astonishing: flame propagation in such a mixture must approach a sensitized decomposition flame of nitrous oxide. At reduced pressures (70 mm of mercury) in the present apparatus the limits are much narrower (17 to 44·5 per cent NH$_3$ at 60°C).

Maximum burning velocities were found in the present experiments to occur in mixtures slightly on the lean side of stoichiometric—at 38 per cent NH_3—though the velocity for the stoichiometric mixture was very close to the maximum. The same location of $S^{max.}$ was made qualitatively by W. G. PARKER and H. G. WOLFHARD[4] and quantitatively by P. AUSLOOS and A. VAN TIGGELEN[3] and by J. WONTERGHEM and A. VAN TIGGELEN[22] (at 38 and 37·5 per cent NH_3 respectively). Maximum flame temperature was found[16] in a rich mixture (41·5 per cent NH_3) though the value measured (2 620°K) was about 160° below the adiabatic value. If this location is correct, it would call for a different explanation from that offered for a parallel case by A. G. GAYDON and H. G. WOLFHARD[13] who discuss oxygen–ammonia mixtures in terms of the relative heats of formation of the fuel and oxidant.

The values found for the maximum velocity $S_U^{max.}$ from previous burner measurements at 1 atm are 72·5 cm sec^{-1} and 92 cm sec^{-1} (values based on visible[3] and schlieren[16] photography respectively) and 80 cm sec^{-1}. This last value comes from a graph[4] of S_U versus P; from the same graph a value of ca. 65 cm sec^{-1} for $S_U^{max.}$ at 70 mm may be read—though the authors consider errors of ± 30 per cent possible. In the present experiments, the value of S_U derived is 79 cm sec^{-1} in the 38 per cent ammonia mixture. Thus, no significant differences are revealed between this result and those for atmospheric pressure. Coupled with the smallness of the pressure dependence of S_B in the bomb measurements reported here, this again implies an effective overall reaction order n of 2.

The isothermal reaction kinetics are complex. Pressure/time measurements by A. VOLDERS and A. VAN TIGGELEN[24] at temperatures in the neighbourhood of 530°C lead to a reaction of order ca. 1 in nitrous oxide and ca. zero in ammonia. The activation energy is ca. 47 kcal mole^{-1}, close to that (48 kcal mole^{-1}) found[24] for N_2O pyrolysis in the same apparatus. The overall activation energy derived from measurements on the flame has been reported[25,16] as 61·5, 51·5 and 65·5 kcal mole^{-1} respectively.

Nitric oxide–ammonia flames

There appear to be no previous reports of conventional flammability limits for nitric oxide–ammonia mixtures. G. K. ADAMS and G. W. STOCKS reported[18] that mixtures containing from 23·5 to 73·5 per cent NH_3 would support a flame on a burner at 1 atm. The limits found in the present work (27 to 53 per cent NH_3) at 70 mm of mercury show a narrowing with decreased pressure which is most marked on the rich side.

Flame speeds are greatest on the ammonia-rich side, the maximum velocity S_B at 70 mm of mercury occurring in a mixture containing 45 per cent NH_3. G. K. ADAMS and G. W. STOCKS had difficulty in making reproducible measurements near to these proportions and located the maximum velocity at 1 atm at 40 per cent NH_3: their diagram[18], however, is equally consistent with a maximum at 45 per cent NH_3. They calculated[18] burnt gas temperature, finding a maximum value (2 960°K) in a lean mixture (37 per cent NO). H. G. WOLFHARD and W. G. PARKER measured[17] flame temperature in a stoichiometric mixture at 1 atm as 2 910°K, in close agreement with a theoretical value of 2 950°K.

Values for flame speeds S_U at 1 atm in stoichiometric mixtures of ca. 70 cm sec^{-1} and ca. 85 cm sec^{-1} have been reported[4,18], neither value claiming high precision. A rate for S_U at 70 mm of ca. 65 cm sec^{-1} in the stoichiometric mixture may be read from a graph[4], in agreement with the value of 62·5 cm sec^{-1} (cf. maximum velocity 65 cm sec^{-1}) found in the present work.

There are again no significant differences between burning velocities at low pressures and at 1 atm and this corresponds to an effective reaction order n of 2.

The isothermal kinetics have been examined by C. P. FENIMORE and J. R. KELSO[26], H. WISE and M. F. FRECH[27], A. VOLDERS and A. VAN TIGGELEN[28], and D. R. POOLE and W. M. GRAVEN[29]. Oxidation by nitric oxide requires higher temperatures than nitrous oxide or oxygen; the kinetics are complicated and experimental findings conflicting. Activation energies

(kcal mole^{-1}) of: 70, 54·7, 50 and 58·4 have been reported[26–29].

Intercomparisons of Oxygen, Nitrous Oxide and Nitric Oxide as Oxidants and of Hydrazine and Ammonia as Fuels

Differences between the three oxidants are revealed in range of flammability, location and magnitude of maximum flame speeds and in susceptibility to quenching. To compare compositions in different systems logically, simple percentages have to be replaced by a fuel–oxidant balance (F/O) relative to that in a stoichiometric mixture $(F/O)_{st.}$. The most convenient is the reduced richness* denoted by the symbol R and defined by the relation

$$R = \frac{(F/O)}{(F/O) + (F/O)_{st.}}$$

having values between zero (pure oxidant) and unity (pure fuel), being 0·5 in the stoichiometric mixture. If the percentage of ammonia in a mixture with oxygen is p then for that mixture R is $3p/(400-p)$, and if the percentage of ammonia in a mixture with nitrous oxide or nitric oxide is q then R is $3q/(200+q)$. In these terms, the lean and rich composition limits of flammability and the locations of maximum flame speeds are as set out in Table 3. It will be seen that, at low pressures, nitrous oxide is as good a supporter of ammonia combustion as oxygen—and a better one in lean

consequence of different energy releases and heat capacities of products, final flame temperatures are very close, the nitric oxide flame being hottest. The flame speeds S_B, however, fall from ca. 1 250 cm sec^{-1} for oxygen mixtures through ca. 900 cm sec^{-1} for nitrous oxide to ca. 700 cm sec^{-1} for nitric oxide. The values of S_{U} behave similarly, emphasizing even more the superiority of oxygen. However, although nitric oxide is least reactive, the differences between it and oxygen are far less in ammonia combustion than they are in the combustion of hydrocarbons, hydrogen and carbon monoxide.

The degree of dilution by inert gases which the different flames will sustain shows (Table 1) the same pattern. Flames can be propagated in all three systems in mixtures containing up to 40 mm of mercury partial pressure of argon. Nitrogen prevents propagation when its partial pressure is above 30 mm in NO mixtures and above 35 mm in N$_2$O mixtures. Helium extinguishes all flames, partial pressures of 5 mm of mercury being enough for NO mixtures, 10 mm for N$_2$O, and 25 mm for oxygen.

Rather unexpectedly, the effect of reduced pressures operates differently, for stoichiometric ammonia–oxygen flames could not be burned at pressures below 63 mm of mercury, while nitrous oxide and nitric oxide flames burned down to 49 and 56 mm respectively. These extinction pressures are quenching phenomena and it is the case[13] at 1 atm that the quenching diameter for ammonia–oxygen

Table 3. Intercomparison of O$_2$, N$_2$O and NO in terms of reduced richness R

	O$_2$ + NH$_3$	N$_2$O + NH$_3$	NO + NH$_3$
R at limits (70 mm Hg)	0·21 to 0·55	0·23 to 0·55	0·36 to 0·63
R at limits (760 mm Hg)	0·125 to 0·74	0·04 to 0·81	0·31 to 0·80
Location of S_B (max.)	0·43	0·48	0·55

mixtures at 1 atm. While nitric oxide is less good absolutely, it is relatively a better supporter of combustion in rich mixtures than in lean.

The burning velocities (Table 2) mirror the relative reactivities of the three oxidants. As a

*Adapted from R. C. Murray and A. R. Hall; elsewhere H. G. Wolfhard has in effect used the reduced leanness $r_{m} = 1 - R$.

flames is larger than for ammonia–nitric oxide.

When flame speeds in the combustions of ammonia and hydrazine are compared (Table 4) there are evident quantitative contrasts. Hydrazine is an endothermic compound and can support a flame in decomposition so that flammability persists to values of $R = 1$ in pure hydrazine. Because hydrazine is endothermic,

Table 4. Exothermicities, flame speeds and flame temperatures in hydrazine combustion

System and stoichiometry $(T_U=62°C;\ P_U=40\ mm\ Hg)$	$-\Delta H_{298}$ kcal per mole N_2H_4	T_B $(°K)$	S_B $(cm\ sec^{-1})$	S_U $(cm\ sec^{-1})$
$N_2H_4+O_2=N_2+2H_2O$ $(R=0.5)$	138·3	2 700	4 020	280
$N_2H_4+2N_2O=3N_2+2H_2O$ $(R=0.5)$	177·5	2 655	2 400	164
$N_2H_4+2NO=2N_2+2H_2O$ $(R=0.5)$	181·5	2 745	3 150	245
$N_2H_4+NO=1.5N_2+H_2O+H_2$ $(R=0.67)$	122·1	2 645	3 550	238

flame temperatures are higher—though, as a consequence of dissociation, not greatly so—differences varying from 30° to 75°C. Flames, however, are much faster, values of S_B and S_U being from two to five times as great[5,30] as for ammonia mixtures.

Chemically, the relatively lower reactivity of ammonia can be correlated with three independent factors. First, its homogeneous decomposition occurs much less readily. Secondly, because $D\,(H-NH_2)$ is more than 100 kcal mole^{-1} whereas $D\,(NH_2-NH_2)$ is[31] about 57–60 kcal mole^{-1}, ammonia is a less prolific source of amino radicals. Thirdly, ammonia is less susceptible to free radical attack, hydrogen abstraction from NH_3 requiring[32] nearly twice the activation energy as abstraction from N_2H_4. However, it is noteworthy that whereas maximum flame speeds occur in the stoichiometric mixtures $N_2H_4+O_2$, $N_2H_4+2N_2O$ just as they occurred in slightly lean ammonia mixtures, in combustion supported by nitric oxide the maxima occur in rich mixtures both for hydrazine $(R_m=0.67)$ and ammonia $(R_m=0.55)$.

References

1 See PARTINGTON, J. R. and PRINCE, A. J. *J. chem. Soc.* 1924, **125**, 2018
2 MURRAY, R. C. and HALL, A. R. *Trans. Faraday Soc.* 1951, **47**, 743
3 AUSLOOS, P. and VAN TIGGELEN, A. *Bull. Soc. chim. Belg.* 1951, **60**, 433
4 PARKER, W. G. and WOLFHARD, H. G. *Fourth Symposium (International) on Combustion*, p 420. Williams and Wilkins: Baltimore, 1953; ADAMS, G. K., PARKER, W. G. and WOLFHARD, H. G. *Disc. Faraday Soc.* 1953, **14**, 97
5 GRAY, P. and LEE, J. C. *Seventh Symposium (International) on Combustion*, p 61. Butterworths: London, 1959; *Rev. Inst. franç. Pétrole*, 1958, **13**, 443
6 GRAY, P. and SPENCER, M. *Combustion & Flame*, 1963, **7**, 315
7 ARMITAGE, J. W. and GRAY, P. 1963, to be published
8 FERNELIUS, W. C. *Inorganic Syntheses*, Vol. 2, p 126. McGraw-Hill: New York, 1946
9 WEINBERG, F. J. *Optics of Flames*, Butterworths: London, 1963
10 LEE, J. C. *Ph.D. Dissertation*, Cambridge, 1955
11 RALLIS, C. J. and TREMEER, G. E. B. *Combustion & Flame*, 1963, **7**, 51
12 LEWIS, B. and VON ELBE, G. *Combustion, Flame and Explosion in Gases*, 2nd ed. Academic Press: New York, 1961
13 GAYDON, A. G. and WOLFHARD, H. G. *Flames: Their Structure, Radiation and Temperature*, 2nd ed. Chapman and Hall: London, 1960
14 DAMKÖHLER, G. and EDSE, R. *Z. Elektrochem.* 1943, **49**, 178
15 VAN WONTERGHEM, J. and VAN TIGGELEN, A. *Bull. Soc. chim. Belg.* 1955, **64**, 99
16 VAN WONTERGHEM, J. and VAN TIGGELEN, A. *Bull. Soc. chim. Belg.* 1955, **64**, 780
17 WOLFHARD, H. G. and PARKER, W. G. *Fifth Symposium (International) on Combustion*, p 718. Reinhold: New York, 1955
18 ADAMS, G. K. and STOCKS, G. W. *Rev. Inst. franç. Pétrole*, 1958, **13**, 483
19 WHITE, A. G. *J. chem. Soc.* 1922, **121**, 1688
20 COHEN, L. *Fuel, Lond.* 1955, **34**, 123
21 VERWIMP, J. and VAN TIGGELEN, A. *Bull. Soc. chim. Belg.* 1953, **62**, 205
22 STEPHENS, E. R. and PEASE, R. N. *J. Amer. chem. Soc.* 1950, **72**, 1188; 1952, **74**, 3480
23 KERR, J. C. and JONES, E. *J. Soc. chem. Ind., Lond.* 1949, **68**, 31

[24] VOLDERS, A. and VAN TIGGELEN, A. *Bull. Soc. chim. Belg.* 1955, **64,** 736

[25] NENQUIN, G., THOMAS, P. and VAN TIGGELEN, A. *Bull. Soc. chim. Belg.* 1956, **65,** 1072

[26] FENIMORE, C. P. and KELSO, J. R. *J. Amer. chem. Soc.* 1952, **74,** 1593

[27] WISE, H. and FRECH, M. F. *J. chem. Phys.* 1954, **22,** 1463

[28] VOLDER, A. and VAN TIGGELEN, A. *Bull. Soc. chim. Belg.* 1954, **63,** 542

[29] POOLE, D. R. and GRAVEN, W. M. *J. Amer. chem. Soc.* 1961, **83,** 283

[30] HALL, A. R. and WOLFHARD, H. G. *Trans. Faraday Soc.* 1956, **52,** 1520

[31] KERR, J. A., SEKHAR, R. C. and TROTMAN-DICKENSON, A. E. *J. chem. Soc.* **1963,** 3217

[32] GRAY, P. and THYNNE, J. C. J. *Trans. Faraday Soc.* 1964, **60,** 1047