303.   *Properties of the Oxides of Nitrogen.   Part VI.   Flame Propagation in the System Nitric Anhydride–Ozone.*

By (the late) T. M. LOWRY and R. V. SEDDON.

Mixtures of nitric anhydride, ozone, and oxygen were ignited in a long reaction tube, and the time required for the flame to travel along a column 90 cm. long, maintained at a constant temperature, was measured. The speed of the flame is extremely sensitive to changes of conditions : *e.g.*, (*a*) the concentrations of anhydride and ozone and the " age " of the mixtures; (*b*) the temperature of the tube and the total pressure; (*c*) the diameter of the tube and its horizontal or vertical position; (*d*) the nature and concentration of the inert gas.

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PART V (J., 1936, 1409) described a few experiments on the flame produced by igniting a mixture of dinitrogen pentoxide (nitric anhydride) and ozonised oxygen in a long combustion tube; a mechanism was suggested for the reaction, and a few determinations of flame speed made. The present work describes a method for preparing gaseous mixtures of known composition, and a technique for measuring flame speeds accurately. A thorough study was made of the variation of flame speed with (*a*) the " age " of the mixture, (*b*) concentration of ozone or nitric anhydride, (*c*) the temperature of the combustion tube,

(*d*) diameter of tube, (*e*) direction of propagation, *i.e.*, upward, downward, or horizontal, (*f*) the nature and concentration of the inert gas.

The observed results are explained on the basis of a simple kinetic theory involving propagation of the flame by the *diffusion* of " hot " molecules from the flame front into the unburnt gases causing activation and catalysing further reaction. The actual reactions taking place in the flame front, involving the formation of the unstable intermediate product NO_3, will be dealt with in a later paper when the slow reaction between the gases has been investigated.

<div align="center">EXPERIMENTAL.</div>

Preparation and Purity of Materials.—Ozonised oxygen (12% by weight) was prepared from ordinary cylinder oxygen, which was thoroughly dried before and after passing through the ozoniser.

The liquid nitrogen tetroxide used in the preparation of the pentoxide was a specially purified sample supplied in Carius tubes by Imperial Chemical Industries Ltd. (Nobel's section).

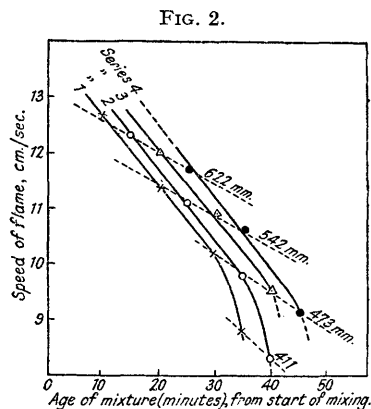<div align="center">FIG. 1.</div>
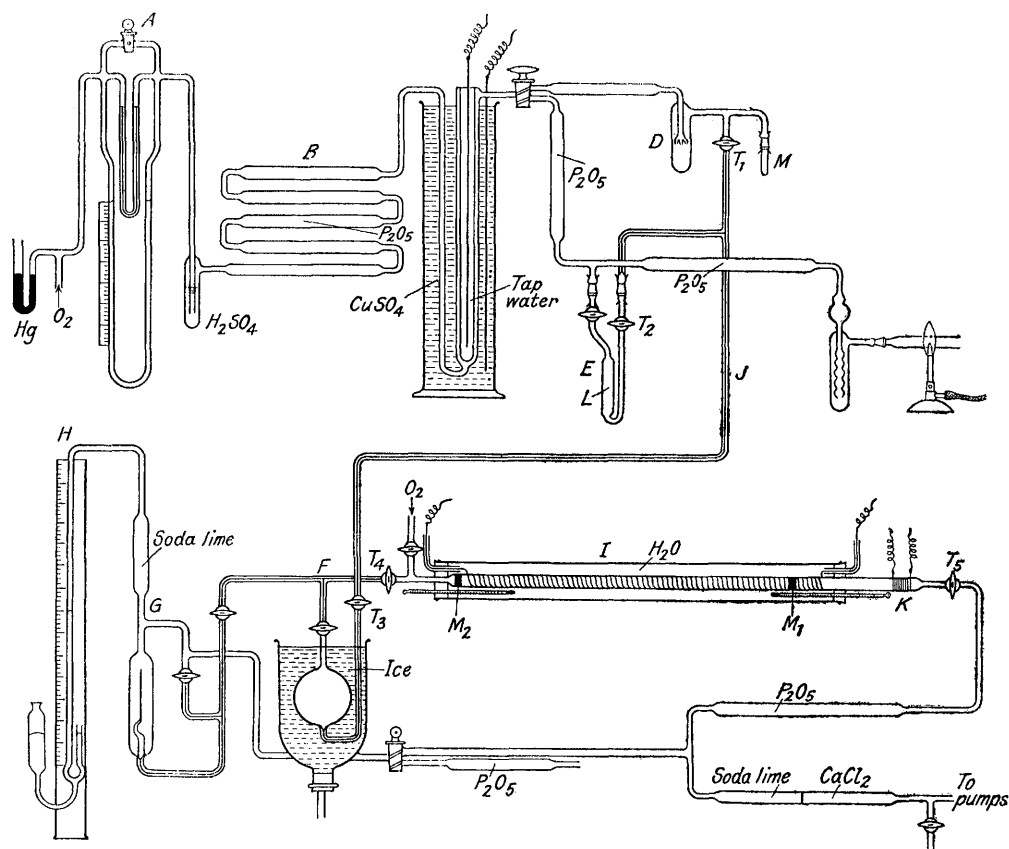
2 or 3 C.c. of this liquid were distilled through phosphoric oxide into the reaction vessel *D* (Fig. 1); the U-tube *E* was attached to the ground glass joint at *M*, ozonised oxygen passed over the tetroxide at room temperature, and the pentoxide formed frozen out into limb *L* of the U-tube by means of solid carbon dioxide in alcohol. Traces of nitrogen peroxide were removed from the pentoxide by allowing the U-tube to warm up, and passing oxygen through until all brown fumes disappeared. The U-tube was then attached to the apparatus as shown, and kept in solid carbon dioxide and alcohol.

A stream of dry oxygen, of known rate of flow, was passed through the U-tube containing the pentoxide kept at constant temperature, and the amount of the pentoxide taken up was

measured by absorption in concentrated potassium hydroxide solution. The "apparent" vapour pressure was calculated for various rates of flow, and the true vapour pressure obtained by extrapolation to zero rate. The values obtained for various temperatures are given below,

Temp.	$-11\cdot0°$	$0\cdot0°$	$10\cdot8°$
Vapour press., mm. { Measured	17	48	139·5
{ Obtained by other workers	17	50	136

being compared in the third line with interpolated values from measurements made by Russ and Pokorny (*Monatsh.*, 1913, **34**, 1051) below 10·5° and by Daniels and Bright (*J. Amer. Chem. Soc.*, 1920, **42**, 1131) above 10·5°.

Preparation of Mixtures of Nitrogen Pentoxide and Ozone, and Measurement of Flame Speeds.— In order to secure definite concentrations of the pentoxide and of ozone, it was necessary to abandon the attempt to saturate ozonised oxygen with the vapour, and to prepare the mixtures in a mixing-bulb surrounded with ice. The apparatus is shown in Fig. 1. The oxygen drying and ozonising system B was essentially the same as that used by Lowry and Lemon (*J.*, 1935, 692). A flow-meter A, using sulphuric acid, was introduced in order to keep careful control over the rate of flow of oxygen through the ozoniser : a good needle valve on the oxygen cylinder enabled this to be done. Careful measurements were made on the variation of the proportion of ozone produced for various rates of flow. The ozone content was found to change by only 1% for a change of 80 c.c./min. in the rate of flow, over the range 0—300 c.c./min. The rate was normally kept constant at 198 ± 3 c.c./min. Measurements were also made on the variations caused by change of voltage on the ozoniser. The proportion rises to a fairly flat maximum at 7500 ± 8000 volts. Normally the voltage was kept constant at 7500 ± 100 volts, and with the above-mentioned rate of flow of oxygen the ozone content was 11·1% by weight. Since a mercury manometer cannot be used directly with these highly corrosive gases, a Bourdon gauge G, used as a null instrument, was inserted between the mixing bulb F and the manometer H. The mixing bulb (1 l. capacity) was kept in melting ice. The reaction vessel I was a long, soda-glass tube of 11·7 mm. internal diameter, wound with a nichrome heating coil and surrounded by a water jacket. The temperature of the jacket read on two thermometers was constant to 0·1°, and was maintained at 20°. A small heating coil K was used for igniting the gas mixture. The apparatus was washed out with dry oxygen, and could be evacuated down to 1 cm. pressure by means of two filter pumps.

Manipulation was as follows. The reaction tube, mixing bulb, gauge, manometer, and U-tube were evacuated down to 1 cm. pressure; stopcock T_4 was closed and the U-tube allowed to warm up until the required pressure of nitric anhydride (usually 30 mm.) was attained in the mixing bulb; T_3 was then closed, and the stock of anhydride again frozen. The ozoniser was started, and the rate of flow of oxygen and the applied voltage carefully regulated to the normal working values mentioned above. With stopcock T_2 open, ozonised oxygen was slowly drawn off at J from the main stream, T_3 being used for control. It required 5 minutes to obtain a pressure of 675 mm. of ozonised oxygen equivalent to 50 mm. of ozone. On the ninth minute, stopcock T_5 was closed, and the mixture admitted to the reaction tube; then T_4 was closed, and the mixture ignited on the tenth minute. The time for the flame to travel from mark M_1 to M_2, 90 cm., was measured with a stop-watch reading to 0·2 second. The reaction tube was immediately evacuated, and a second charge of mixture admitted on the 14th and ignited on the 15th minute. Four or five "runs" could be done before the total pressure or ozone content became too low to give the flame.

A test was made on the uniformity of movement of the flame. A mark M_3 was made on the combustion tube equidistant from M_1 and M_2, and the velocity of the flame measured over the first and the second half of the run by means of two stop-watches. The speeds were identical.

Age of Mixtures.—In order to determine the effect on the flame speed of the progressive decomposition of the mixture, the mixing bulb was charged initially with 30 mm. of nitric anhydride, to which ozonised oxygen was added to give 50 mm. of ozone, with oxygen to a total pressure of 715 mm. On admission of this mixture to the exhausted combustion tube, the pressure in the tube fell in successive experiments to 622, 542, 473, and 411 mm., and the velocity of the flame was measured at each of these pressures. The influence of age was then determined by beginning further series of experiments after increased intervals from the moment when ozone was first admitted to the bulb.

The results are shown graphically in Fig. 2. Each result is the average of three measurements which did not differ by more than 0·3 cm./sec. When points representing equal pressures

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in different series are joined, the velocity of the flame is seen to fall off in a linear manner with the age of the mixture; but whereas at 622 and 542 mm. the decrease is constant at about 0·06 cm./sec. for each minute of ageing, this rate increases to about 0·08 at 473 mm. pressure and to 0·11 at 411 mm. The results thus obtained were confirmed by measurements in which the pressure in the first of a series of experiments was reduced to 542, 473, or 411 mm.

Influence of Concentration of Ozone on Speed of Flame.—The velocity of the flame is extremely sensitive to the concentration of ozone. In two series of experiments 30 mm. and 15 mm. of pentoxide were mixed with ozonised oxygen to a maximum of 50 mm. of ozone, which was then reduced by 1 mm. steps by adding oxygen in place of ozonised oxygen. The flame speed was then determined for a series of pressures, and corrected for the ageing of the mixtures. In correcting these and all other results, the zero time was taken as $2\frac{1}{2}$ mins. from the start of mixing, since the completion of this process required 5 mins. The results are shown in Fig. 3, where the flame speed is plotted against the pressure of ozone for various values of the total pressure. The upper series of curves are for 30 mm. of pentoxide, and the lower series for 15 mm. The effects are remarkable, since with 30 mm. a reduction of only 5 mm. in the pressure of ozone reduces the velocity of the flame from 12·5 cm./sec. to 9·8 cm./sec. at a total pressure of 622 mm., and all the other curves show a still more rapid decrease of velocity as the partial pressure of the ozone is reduced.

FIG. 2.

Influence of ageing on speed of flame.

The upper portions of the curves tend towards straight lines, but fall off more and more rapidly as the ozone content decreases, until finally the flame can no longer be propagated at velocities less than 8 cm./sec. The curves for 15 mm. of pentoxide resemble the lower portions of the curves for 30 mm.

Calculation shows that the fall of velocity with the age of the mixture may be attributed directly to loss of ozone. It has already been shown (above) that at a total pressure of 622 mm.

FIG. 3.
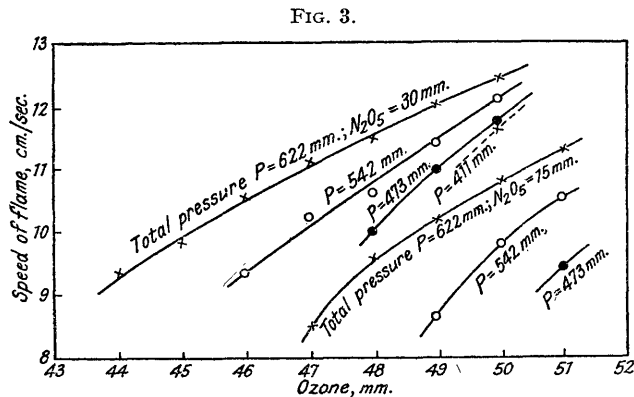
Influence of concentration of ozone on speed of flame.

with 30 mm. of pentoxide and 50 mm. of ozone the speed of the flame falls off at the rate of 0·06 cm./sec. in each minute, whilst the ozone content falls off at the rate of 0·14 mm./min. (from later work on the " slow reaction "). Division of the first by the second shows that the reduction in the flame speed for 1 mm. loss of ozone should be $0·0610 \div 0·14 = 0·43$ cm./sec. The experimental figure, *i.e.*, the gradient of the 622-mm. curve in Fig. 3, is found to be 0·4—0·45 cm./sec.

Influence of Concentration of Nitric Anhydride.—Nitric anhydride (10—50 mm.) was admitted to the mixing bulb, and then ozonised oxygen to give 50 mm. of ozone. Not less than two concordant determinations of flame speed were made for each set of pressures. The results are shown graphically in Fig. 4. The corrected velocities rise to a maximum at a concentration of pentoxide which is almost constant at about 30 mm., *i.e.*, rather more than one half of the partial pressure of the ozone.

It seems clear that the very rapid rise in flame speed at the beginning is due to the increasing amount of " fuel," all of which is burnt up. With a fixed amount of ozone, only a definite quantity of the anhydride can be consumed, and any excess merely acts as inert gas, resulting in the flattening out of the curves.

Influence of Temperature on Speed of Flame.—A first series of experiments with the optimum mixture was made at 20—40° under pressures of 622, 542, and 473 mm. The velocity fell off slowly from a flat maximum at about 20°, until the temperature reached 30°, after which it decreased very rapidly indeed, because of rapid destruction of ozone in the reaction tube in presence of nitric anhydride prior to ignition.

After this series of measurements had been completed, it was found that the values at 20° were no longer reproducible, until the tube had been taken down and washed with nitric acid and water as before. It is to be concluded that the surface plays a part in determining the flame speed, and that heating changes the properties of the surface.

The reaction tube was cooled by circulating water through the outer jacket, and a second series ranging from 0—30°, after the tube had been washed out with nitric acid, gave concordant results, but these were a little lower than those of the first series. They show a well-marked maximum at about 20°, but fall off rather less steeply at lower than at higher temperatures. Several months separated the two sets of results, and there had been a gradual drift in the absolute values obtained, probably due to the changing surface conditions. The results are plotted in Fig. 5.

FIG. 4.

Influence of concentration of N_2O_5 *on speed of flame.*

Influence of Diameter of Tube on Speed of Flame.—The main series of observations was made with tubes of different diameter selected from a uniform batch of soda-glass. In order to secure

FIG. 5.

Influence of temperature on speed of flame.
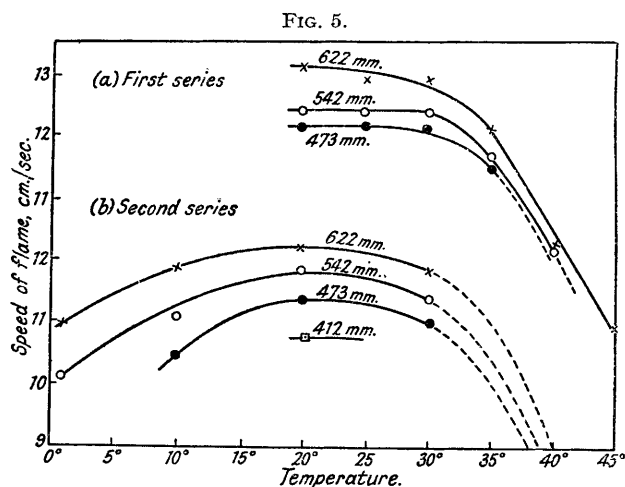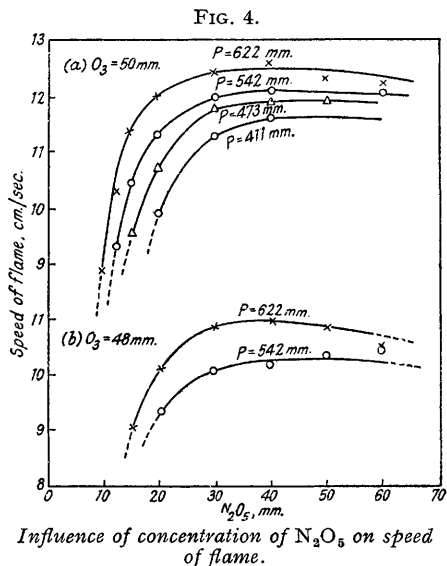
a uniform surface the tubes were washed with (i) concentrated nitric acid, (ii) tap water, (iii) distilled water, and (iv) methyl alcohol, and then dried in a current of air. The tube was sealed on to the apparatus, washed with dry oxygen and evacuated twice, then filled with oxygen and allowed to stand overnight. Even with this standardised treatment, the results obtained were rather variable, but they show that the flame speed is approximately directly proportional to the diameter of the tube. The internal diameters of the tubes ranged from 13·45 to 8·40 mm.; the flame, however, could not be produced in tubes of less than 10 mm. diameter. Some experi-

ments were carried out in soda-glass tubes of similar diameter but from different lots of glass. The results obtained bore no relation to the main series.

Flame Speeds in Upward, Downward, and Horizontal Directions.—The tubes used in the preceding experiments were cleaned and used again, first in a vertical position then horizontally. The velocity of the flame in the downward direction is two-thirds of that in the upward direction on account of convection. The downward velocity decreases with the diameter of the tube, but the upward velocity is independent of diameter. The results in the horizontal tubes are similar to those for upward propagation, but in the largest tube (13·45 mm.) the velocity horizontally is definitely greatest.

The Influence of the Inert Gas on the Flame Speed.—An apparatus was constructed for the preparation of liquid ozone, similar to the one used by Norrish and Neville (J., 1934, 1864). It

FIG. 6.

Effect of inert gas on speed of flame.
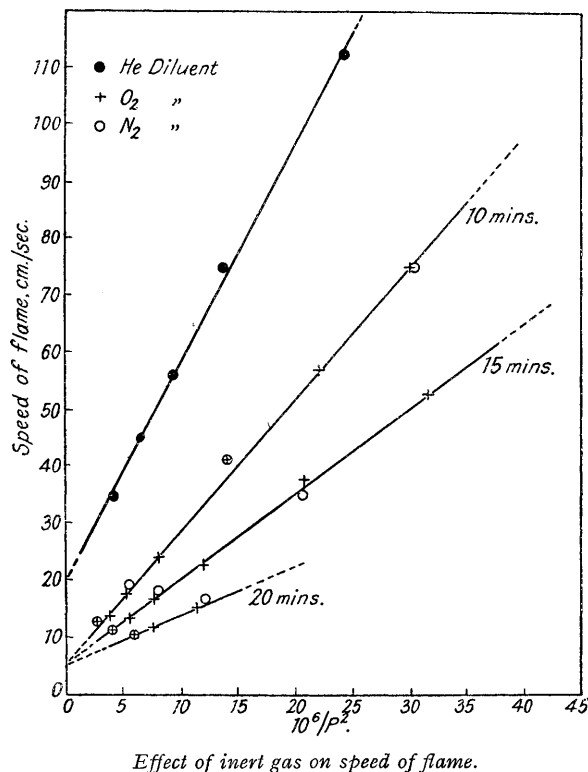
was attached to the main apparatus (Fig. 1) at M, so that mixtures containing a higher percentage of ozone could be obtained. The liquid ozone was analysed before use, and the ozone content found to vary from 80 to 85% with different preparations. It was now possible to obtain mixtures of ozone and nitric anhydride with any desired pressure of oxygen or other inert gas. The nitric anhydride was admitted to the bulb first, then the highly concentrated ozone, and lastly various amounts of oxygen, nitrogen, or helium. The flame speeds for these mixtures were measured in the usual way; they are plotted against the reciprocal of the square of the total pressure in Fig. 6. The lowest three curves are for mixtures ignited on the 10th, 15th, and 20th minutes respectively. The flame speed rises rapidly as the amount of inert gas decreases and is inversely proportional to the square of the total pressure. With nitrogen and oxygen, the flame speeds are identical, but with helium they are much greater at corresponding pressures. Bone and Outridge (*Proc. Roy. Soc.*, 1936, *A*, **157**, 234) recently obtained similar results for mixtures of acetylene or ethylene and oxygen with the inert gases nitrogen and argon : the flame speeds rapidly increased as the amount of inert gas in the mixture decreased.

The Luminous Flame.—At the lowest pressures used, *i.e.*, when no inert gas had been added, the mixture could not be ignited in the usual way. If the heating coil K (Fig. 1) was switched

on, nothing happened; when, however, stopcock T_5 was opened and the mixture began to be slowly pumped out, a flame, which was easily seen to be luminous in full daylight, shot along the tube at a speed too rapid to be measured by means of the stop-watch. This luminous flame was examined in the dark, and it was found that mixtures containing quite large amounts of inert gas also gave a luminous flame. All the latter mixtures could be ignited directly by the heating coil K. Tests on the quenching of this luminosity showed that a mixture containing 30 mm. of anhydride, 50 mm. of ozone, and 414 mm. of oxygen (total pressure, 407 mm. when admitted to the reaction tube) gave a flame which could not be detected with the naked eye in the dark. A mixture containing 30 mm. of anhydride, 50 mm. of ozone and 314 mm. of oxygen, which gave a pressure of 324 mm. in the reaction tube, gave a flame which could only just be detected as a very faint, hemispherical, yellow glow in the dark. A mixture of the same composition but with helium instead of oxygen gave a flame easily seen in the dark. The blue band could still be seen at the flame front even when the luminosity was present. It seems probable that the luminosity is due to reaction products, *i.e.*, nitrogen dioxide, excited by the energy liberated in the reaction, while the quenching of the luminosity is to be ascribed to the rapid dissipation of the energy by the inert gas. Oxygen, with a larger number of degrees of freedom, is far more effective in this respect than helium.

DISCUSSION.

The greater flame speed in the upward than in the downward direction is accounted for by convection, and shows that a considerable amount of heat is evolved in the reaction.

The flame speed is very sensitive to small changes in the ozone concentration, and under the conditions of the experiments the flame could not be obtained with mixtures containing less than 44 mm. of ozone as compared with a maximum of 50 mm. given by the ozoniser. In the propagation of the flame the ozone is probably activated first, by hot molecules from the flame front, and then reacts with the nitric anhydride. The gradual falling off in flame speed with the ageing of the gas mixture is due to slow destruction of ozone.

The nitric anhydride can be regarded as the " fuel " and as the concentration increases the flame speed rises rapidly, reaches a maximum, and falls off gradually since excess fuel will act as inert gas.

The flame speed is roughly proportional to the diameter of the reaction tube, and the flame cannot be obtained in tubes of less than 10 mm. diameter. The surface has a specific effect and plays a minor part in determining the flame speed, possibly by acting as an acceptor of excess energy from the hot molecules.

The effect of the inert gas and the rapid rise of flame speed as the pressure decreases can be accounted for on the basis of Fick's law of diffusion (*Pogg. Ann.*, 1855, **94**, 59), *viz.*, $ds = -Dq(dc/dx) \cdot dt$, where ds is the amount of substance which diffuses across an area q in time dt, D is the coefficient of diffusion and dc/dx the concentration gradient of the diffusing gas. The coefficient of diffusion can be approximately expressed as $D = \frac{1}{3}\bar{C}L$, where $\bar{C}$ is the velocity and L the mean free path; L, and hence D, is inversely proportional to the pressure. The gradient of concentration of active molecules at the flame front will also be inversely proportional to pressure; hence the flame speed will vary inversely as the square of the total pressure, in accordance with the observed result. Theory predicts that D will vary as $T^{3/2}$, and at 0° it will increase by a factor of 1·06 for 10° rise in temperature. Experiments on diffusion, however, show that the factor varies from 1 to 1·5, and in our experiments (see Fig. 5) from 0° to 10° the flame speed increases by a factor of 1·2 for the highest pressure. At higher temperatures, unfortunately, measurement of the dependence of flame speed on temperature is vitiated by the instability of the mixture and no accurate estimate of the rate of change can be made. The coefficient of diffusion for oxygen into helium has been shown to be higher by a factor of 3 or 4 than for the same gas diffusing into nitrogen (Loeb, " Kinetic Theory of Gases "). With this fact the higher flame speeds obtained with helium as diluent are in qualitative agreement, the ratio of speeds in helium and nitrogen being approximately 2. It may therefore be concluded that the propagation of the flame is due to the diffusion of " hot " molecules from the flame front into the unburnt gases causing activation and further reaction.

In 1883 Mallard and Le Chatelier expressed the view that flame propagation during the uniform movement is due to " the cold mixture immediately in front of the flame being

raised to its ignition temperature by conduction of heat from the burning and burnt layers immediately behind the flame front." They obtained the following formula for the velocity of flame propagated in this way :

$$V = [L(T - t)/C(t - \theta)][f(T, t)]$$

where T = temperature of combustion, t = ignition temperature, θ = initial temperature, L = thermal conductivity of unburnt gas, C = mean specific heat of the burning or just-burnt gas, and $f(T, t)$ = a constant.

On this formula, however, the effect of removing the inert gas would be to lower the thermal conductivity L of the unburnt gas and cause a decrease in the flame speed. Bone, Fraser, and Winter (" Flame and Combustion in Gases," Bone and Townend) have carried out experiments on the relative effects of helium, argon, and nitrogen on the flame speeds for mixtures of acetylene and oxygen, and obtained similar results to those of Coward and Hess on the methane–oxygen flame. The flame speeds for mixtures containing helium or argon are much greater than for mixtures containing nitrogen, and they attribute this to the difference in thermal conductivity of the mixtures. In the light of our present work, this explanation is open to criticism.

The mechanism that we have deduced for the propagation of the flame is equivalent to an energy chain in which liberated energy is passed on directly from resultants to reactants.

Preliminary investigation of the slow reaction between ozone and nitric anhydride showed that the mixture contained NO_3, which is probably the intermediate product in the catalysed decomposition of ozone. The reactions involved must closely resemble those taking place in the flame, and these will be discussed when the slow reaction has been thoroughly investigated.