Summary

An apparatus, with mercury as the confining liquid, for measuring by the static method dissociation pressures of compounds giving a condensable vapor, has been described.

Temperatures were measured by the thermocouple-potentiometer method with the cold junction at 0°.

Equilibrium was reached from higher temperatures and pressures where reactions were found to be feasibly reversible as indicated in the tables.

The dissociation pressures of the following closed systems have been measured: $xK_2H_2P_2O_7 \overset{\Delta}{\rightleftharpoons} 2(KPO_3)_x + xH_2O$; $xNa_2H_2P_2O_7 \overset{\Delta}{\rightleftharpoons} 2(NaPO_3)_x + xH_2O$; $xKH_2PO_4 \overset{\Delta}{\rightleftharpoons} (KPO_3)_x + xH_2O$; $2NaH_2PO_4 \overset{\Delta}{\rightleftharpoons} Na_2H_2P_2O_7 + H_2O$.

No equilibrium-pressure relations in the closed systems, $2KH_2PO_4 \overset{\Delta}{\rightleftharpoons} K_2H_2P_2O_7 + H_2O$ and $xNaH_2PO_4 \overset{\Delta}{\rightleftharpoons} (NaPO_3)_x + xH_2O$, were obtained in the temperature ranges studied.

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[CONTRIBUTION FROM THE BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE, AND THE SAFETY IN MINES RESEARCH BOARD, BRITISH MINES DEPARTMENT]

MECHANISM OF THE UNIFORM MOVEMENT IN THE PROPAGATION OF FLAME[1]

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When an inflammable gas mixture is ignited at the open end of a tube closed at the other end, flame is propagated at first at uniform speed. In weak mixtures this "uniform movement" may persist during the whole passage of flame throughout the tube, but in most cases the uniform movement sooner or later gives place to a vibratory movement which may either develop into detonation or result in spontaneous extinction of the flame during some particularly violent vibration.[4]

When ignition is effected near the *closed* end of a tube, flame is propagated toward the open end at an accelerated rate which may ultimately

[1] This is a joint report on one of a series of investigations to decrease accidents in mines, being conducted under the coöperation between the Bureau of Mines, U. S. Department of Commerce, and the Safety in Mines Research Board, British Mines. Department. Published with approval of the Director, United States Bureau of Mines.

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[4] Mallard and Le Chatelier, *Ann. Mines*, [8] **4**, 274 (1883).

develop into detonation. Vibrations have been observed during the stage of accelerated movement of flame in these circumstances.[5]

A sharp distinction has been drawn by the earlier investigators, Berthelot and Vieille, Mallard and Le Chatelier, and H. B. Dixon, between "l'onde explosive" or the detonation wave, and all other modes of flame propagation. Detonation is not, as looser writers have lately seemed to think, merely an explosion accompanied by a sharp "knock"; it is a mode of propagation of combustion characterized by a constant and maximum speed for each mixture capable of "detonation." The theory is that detonation is transmitted as a discontinuous "shock wave" maintained by the chemical energy of reaction of the medium traversed.[6]

The uniform movement, the accelerated movement, and the vibratory movement of flame are grouped together as dependent essentially on transmission of heat by conduction from the flame front to the neighboring unburnt layer of gas. Mallard and Le Chatelier regarded the uniform movement as the "normal" mode of flame propagation; accelerated and vibratory movement were evidences of complications introduced by bodily movement of the gas mixture.

W. Mason and R. V. Wheeler[7] have critically examined Mallard and Le Chatelier's view of the uniform movement as the "normal" mode of flame propagation by simple conduction of heat. The latter writers had concluded from their observations that as tube diameter was increased to 2 or 3 cm., the speed of uniform movement (for any one gas mixture) approached a constant value, the "normal" speed. Mason and Wheeler determined the speeds for a series of methane-air mixtures in a number of tubes of widely differing diameters; the speeds throughout the series did not increase much, relatively, when the tube diameter was increased from 5 to 9 cm. and it seemed possible that flame was transmitted "normally" in the 9cm. tube; with further increase in diameter, however, the flame speeds again increased and, moreover, visible signs of turbulence were observed in the flame fronts in these larger tubes. Hence, in the wider tubes convection effects were assisting the propagation of flame which, therefore, did not travel by conduction alone.

Mallard and Le Chatelier's conclusions were based on experiments in tubes placed horizontally. Mason and Wheeler argued that convection effects would tend to be eliminated when flame traveled downward through tubes placed vertically, because the hotter gases are then always above the cooler. They observed, for each member of the same series of methane-air mixtures, that flame traveled more slowly downward than horizontally; but even in downward propagation of flame an increase in diameter of tube

[5] Mason and Wheeler, *J. Chem. Soc.*, **117**, 36 (1920).

[6] Jouguet, "Mécanique des Explosifs," G. Doin, Paris, **1917.**

[7] Mason and Wheeler, *J. Chem. Soc.*, (a) **111**, 1044 (1917); (b) **117**, 1227 (1920).

from 5 to 23 cm. gave rise to a greater speed of flame. They conclude, "the enhanced speeds of the flames as they travel downward in the larger tube are, no doubt, due to turbulence of the flame front engendered by convection or eddy currents.... In so far, therefore, as the term 'uniform movement' of flame has been held to be the normal propagation of flame by conduction of heat, it ought to be discarded. The term is, however, a useful one, and fittingly describes a phase in the propagation of flame (obtainable under a variety of conditions, which should be specified) the identification and measurement of which is of considerable value. As a name, without implying a mode of heat transference during the phenomena it describes, there is no reason why it should not be retained, and it may be convenient to do so."

These observations raise the question as to whether conduction of heat is a factor in the propagation of flame, or whether some other mechanism, such as radiation of some type, must be postulated. S. C. Lind[8] has, indeed, based an explanation for Wheeler's[9] observations on the ignition of some paraffin hydrocarbons, on the hypothesis: "....if it is permissible to assume flame propagation to be due to the radiation of energy in some form which is subject to a non-selective absorption roughly proportional to the density of the gaseous medium."

An Experimental Test of the Mechanism of Flame Propagation

When an explosive gas mixture is mixed in the same proportion with each of two inert gases of equal heat capacities—for example, argon and helium—then the resultant mixtures will be identical in the following properties: (1) heat of combustion (of equal volumes, at the same temperature and pressure); (2) heat capacity, and therefore (3) temperature of products of combustion, if the heat losses are equal; and (4) rate of combustion, if the temperatures of combustion are equal. The outstanding differences between the two mixtures, in respect to flame propagation, are that the helium mixture has a much higher thermal conductivity than the argon mixture,[10] and a much lower absorptive power for such a form of radiated energy as Lind suggested might be responsible for flame propagation. A comparison of the speeds of flame in such mixtures should, therefore, test the theories of flame propagation in modes other than that of the explosive, or detonation, wave, for if thermal conduc-

[8] Lind, *J. Chem. Soc.*, **125**, 1867 (1924).

[9] Wheeler, *ibid.*, **125**, 1858 (1924).

[10] This has not been demonstrated experimentally for flame temperatures, nor even for ordinary temperatures; from what is known of the thermal conductivities of mixtures and of the temperature coefficients of thermal conductivities, and from the kinetic theory of gases, the general statement made above can hardly be doubted. This conclusion has received support from some observations, made by the writers, on the relative rates of loss of heat from a platinum wire maintained at a high temperature in mixtures which contained argon and helium in equivalent amounts.

tivity is the important factor of these two, then flame should travel much faster in the helium mixtures than in the corresponding argon mixtures. If the absorptive power for radiated energy is the important factor, however, the reverse should be the case as regards flame speeds, on the reasonable assumption that the energy absorbed by the inert gas is at once available for the combustion reaction.

Experimental Method

Flame speeds were determined by the photographic method used by Mallard and Le Chatelier[4] with modifications by Mason and Wheeler[5] to determine, with the aid of a quartz lens and window, the speeds in less actinic mixtures. The progress of the flame was recorded on highly sensitive bromide paper (Lumière) on a revolving drum whose speed was determined at the same time by photographing break sparks produced with the aid of a tuning fork of known frequency.

The argon and helium used were both of 96.5% purity; the remainder was nitrogen.

Experimental Results

A series of mixtures of methane with "atmospheres" of (a) air, (b) 20.9% of oxygen, 79.1% of argon, (c) 20.9% of oxygen, 79.1% of helium, was made to cover the whole range of inflammability, from lower to higher limit, in each atmosphere. Photographic measurements of the speed of uniform movement of flame in a horizontal tube, 2.5 cm. in diameter, were made for each mixture. Fig. 1 shows the results obtained. The difference between the speeds in air on the one hand, and in mixtures of the same oxygen content but containing argon or helium on the other, is largely explainable by difference in heat capacities of the mixtures; in air the flame temperatures are much lower than in the other "atmospheres" for equal amounts of methane in the three cases; hence, not only is the temperature attainable by the unburnt layer lower, but also the energy gradient between flame and unburnt mixture is less steep in air, energy would be transmitted more slowly, and therefore flame would travel more slowly. The greater interest is, however, in a comparison of the results for argon and helium mixtures; for equal amounts of heat are produced on combustion, and the heat capacities of the mixtures are the same. Flame travels more rapidly in the helium mixtures than in the corresponding argon mixtures, presumably because of the influence of the higher thermal conductivity of helium. However, the difference is not so great as might be anticipated, because the thermal conductivity of helium is more than eight times that of argon, and the mixtures tested contained about three-fourths of their volume of the inert gas.[11]

[11] Fig. 1 shows also that the range of inflammability of the mixtures containing helium is much narrower (from about 5.6 to 14.3% of methane) than the range when argon is the inert gas (from about 4.4 to 15.8% of methane). A similar case has been

To obtain further information, a similar series of experiments was conducted in a wider tube, 5 cm. in diameter. The speeds of flame were increased thereby; the maximum speeds in each atmosphere were found

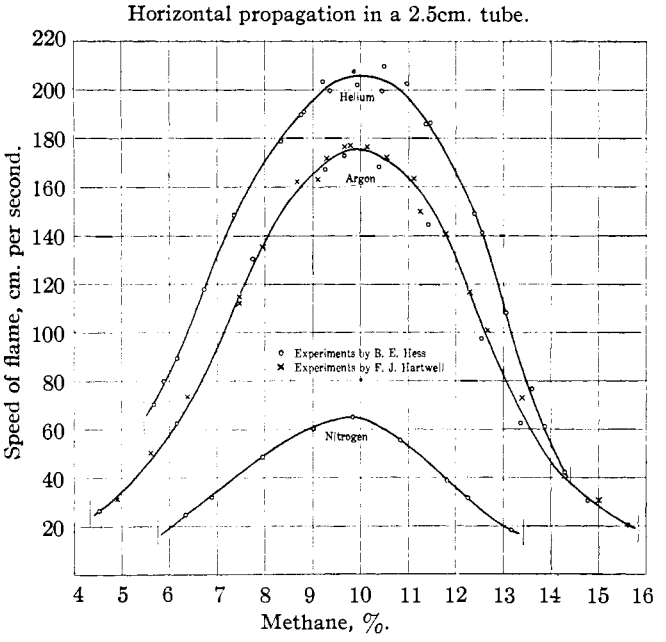

Fig. 1.—Speed of uniform movement of flame in mixtures of methane with the "atmospheres:" nitrogen (ordinary air), oxygen 20.9%, nitrogen 79.1%; argon (a mixture), oxygen 20.9%, argon 79.1%; helium (a mixture), oxygen 20.9%, helium 79.1%.

at the same composition of mixture, but the speeds in the argon and helium series were much closer than in the narrower tube.

TABLE I

SPEED OF UNIFORM MOVEMENT OF FLAME IN MIXTURES CONTAINING 10% OF METHANE AND 90% OF AN "ATMOSPHERE" COMPOSED OF 20.9% OF OXYGEN AND 79.1% OF EITHER ARGON OR HELIUM

Diameter of tube, cm.	Inert gas present	Speed upward, cm./sec.	Speed horizontally, cm./sec.	Speed downward, cm./sec.
1.25	A	132	132	131
	He	180	178	179
2.5	A	191 (146)	176	174
	He	205	206	199
5.0	A	244	249	231
	He	255	248	240

explained on the grounds that helium tends to dissipate the heat of the flame front, in weak mixtures, by virtue of its high thermal conductivity. [See Coward and Hartwell, *J. Chem. Soc.*, **129**, 1522 (1926).]

A comparison was next made between the argon and helium effects for different directions of propagation of flame, in tubes of different diameters. Owing to the number of observations required, attention was confined in each case to a 10% methane mixture in the atmosphere chosen; this is, for horizontal propagation at least, the mixture of maximum speed of flame. The results are shown in Table I, where each value is the mean of three to six observations, agreeing in most cases within 3% among themselves.

The figures were most consistent in the narrowest tube; in the widest tube the photographs were less satisfactory and the figures somewhat less regular. With suitable allowance for experimental error, the following may be concluded. (1) In the narrowest tube (1.25 cm. in diameter) the speed of flame in the mixtures used is independent of the direction of propagation, but is higher in the helium than in the argon mixtures. (2) In the widest tube (5 cm. in diameter) the speed of flame traveling downward is a little less than the speed in other directions; there is little difference between the speeds in the helium mixtures in comparison with the argon mixtures. (3) In the intermediate tube (2.5 cm. in diameter) the observations may be described in the same terms as for the narrowest tube, except that flame is propagated upward in the argon mixture faster than in any other direction; this case, however, is anomalous in another respect, namely, that several observations grouped themselves around a lower speed (146 cm. per second) of flame. There was no evidence in the photographs that the higher- or the lower-speed flame should be regarded as the normal type. (4) In otherwise identical circumstances, the speed of flame increased regularly with increased diameter of tube used.

Discussion of Results

Although the writers do not claim to give a final explanation for these observations, they offer the following interpretation which is based on their own visual observations of more slowly moving flames, and in part on suggestions provided by the work of Wheeler and collaborators.[7,9]

Flame speeds in methane-air mixtures are such that convection currents give rise to higher speeds for upward and horizontal propagation rather than for downward propagation. In corresponding mixtures of methane with the oxygen-argon and oxygen-helium "atmospheres" used in the present research, flame speeds are much higher as a result of higher temperatures, so much higher, in fact, that the influence of convection currents is negligible in the narrower tubes and nearly so in the widest tube. Hence flame speeds in these mixtures were nearly or quite independent of the direction of propagation.

At the highest speeds, namely, those attained in the 5cm. tube, the substitution of argon for helium has the least effect on flame speeds; in the

narrowest tubes the substitution has the greatest effect. Now the explanation generally advanced for lower speeds observed in narrower tubes is based on the cooling effect of the walls of the tube on the flame; at first sight, it might be thought that mixtures containing helium would be cooled more than those containing argon and, therefore, that the helium mixtures would be more affected than the argon mixtures by reduction in diameter of tube, and that their speeds would be reduced more rapidly by narrowing the tube. This is not so. The high thermal conductivity of the helium mixtures insures them a faster flame in a narrow tube; however, at the very high speeds of the wider tubes the thermal conductivity is not the important factor in determining the *relative* rates in argon and helium mixtures. The important factor, the slow process which determines the relative speeds, is, we suggest, the rate of chemical reaction itself.

Whatever may be the true explanation of the differences, however, it appears that the substitution of helium for argon has, in the various experimental conditions described, either no effect on flame speeds (for example, in the 5cm. tubes) or an effect which is disproportionately small in comparison with the change in thermal conductivity of the mixture (for example, in the narrower tubes). The conclusion is that in the case of methane the important factors in determining the speed of the uniform movement of flame are the flame temperature, which determines the general shape of the speed curves, and the rate of combustion; whatever the precise mechanism whereby energy is transferred from the flame front to the neighboring unburnt layer of gas, this mechanism functions so rapidly that the speed of flame is mainly determined by the other factors named.

Further Comparison between the Effect of Argon and Helium on Flame Speeds

In certain cases the speed of flame may be somewhat higher in argon mixtures than in corresponding helium mixtures. This conclusion was drawn from some experiments by Coward and Hartwell[11] in which the influence of these gases on the limits of inflammability of methane in air were determined for upward propagation of flame in a tube 5 cm. in diameter. It was observed that the limits were narrowed more rapidly by helium than by argon, and that the speeds of flame in the limit helium mixtures were only slightly higher than in the limit argon mixtures, all of which propagated flame at the same speed as in the limit mixtures of methane with air alone. For example, with 30% of diluent in the "atmosphere," the lower limit was in argon mixtures 4.6% of methane, in helium mixtures 5.6% of methane, and the flame speeds were nearly identical. It was argued that 5.6% of methane with the argon "atmosphere" would propagate flame much faster than the 4.6% limit mixture in this atmosphere and, therefore, faster than the 5.6% of methane in the helium "atmosphere."

Fig. 2 shows the speed of uniform movement in a 2.5cm. horizontal tube over the whole range of inflammability of methane in atmospheres composed of air and either argon or helium; the inert gas was 31.25% of the "atmosphere." The flame speeds in the argon mixtures are greater throughout than in the helium mixtures. Fig. 3 shows similar results for atmospheres containing 20.75% of inert gas, but the most inflammable mixtures in this case have almost identical flame speeds. This proves to be a case intermediate between the results of Fig. 2 and Fig. 1. In Fig. 2, flame was slow, but faster in argon mixtures than in helium mixtures; in Fig. 1, flame was fast, but slower in argon than in helium mixtures.

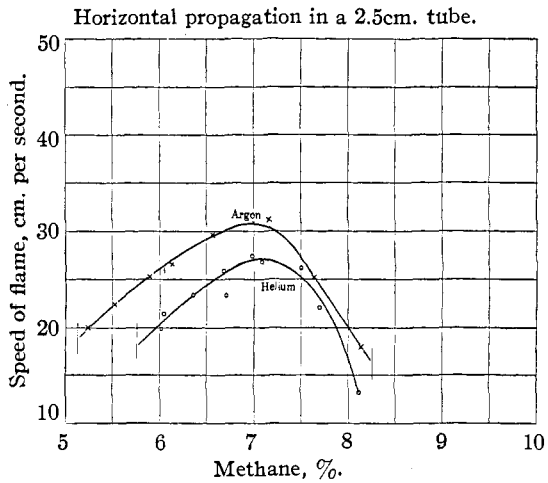

Fig. 2.—Speed of uniform movement of flame in mixtures of methane with the "atmospheres:" argon 31.25%, air 68.75%; helium 31.25%, air 68.75%.

It appears, therefore, as previously discussed, that high thermal conductivity tends to extinguish or slow down the flames in weakly-burning mixtures; in strongly-burning mixtures, high thermal conductivity may in some cases accelerate flame somewhat, but not nearly in proportion to the thermal conductivity.

Experiments recently reported by W. A. Bone, D. M. Newitt and D. T. A. Townsend[12] are the only others known to the writers in which a comparison is made between the effects of argon and helium on the speeds of flame. Their observations concerned the propagation of flame in mixtures of $2H_2 + O_2$ and $2CO + O_2$ with these diluents, under high pressure. They found that the time taken for the attainment of maximum pressure was, for the hydrogen mixtures, always slightly shorter with the helium-diluted than with the argon-diluted knallgas; for the carbon monoxide mixtures,

[12] Bone, Newitt and Townsend, *Proc. Roy. Soc.*, **110A**, 645 (1926).

in some cases those which contained helium exploded more slowly than corresponding mixtures containing argon; in other cases the reverse was observed.

Mallard and Le Chatelier's Equation for the Speed of Uniform Movement of Flame

Mallard and Le Chatelier[4] argued that the speed of uniform movements was given by an equation of the form $v = [L(T - t)/c(t - \theta)]f(T, t)$, in which L is the thermal conductivity of the unburnt gas, T the temperature of the gas after combustion, t the temperature of inflammation, θ the initial temperature of the gas and c the specific heat of the unburnt

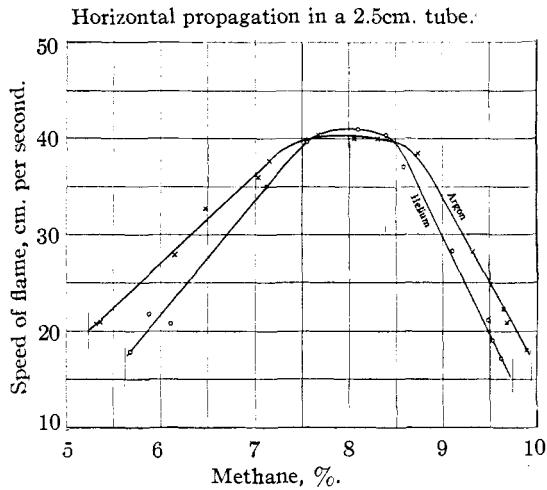

Fig. 3.—Speed of uniform movement of flame in mixtures of methane with the "atmospheres:" argon 20.75%, air 79.25%; helium 20.75%, air 79.25%.

gas. They thought it possible that $f(T, t)$ was a constant. Mason and Wheeler[7a] found that their observed values for v were proportional to $L(T - t)/c(t - \theta)$ for a series of mixtures of methane with air and with atmospheres composed of nitrogen and less oxygen than is present in air, so long as there was more than sufficient oxygen present to burn the whole of the methane, but not otherwise.

In the argon and helium mixtures of the present research, c is constant for mixtures of equal content of inert gas and of methane, and the ratio $(T - t)/(t - \theta)$ is only some 10% different[13] for the more explosive mixtures. Hence, if the formula were correct, the speeds of flame for

[13] The ignition temperature of any one member of the methane-oxygen-argon series is some 30° to 40° lower than that of the corresponding member of the methane-oxygen-helium series. (Private communication, R. V. Wheeler and C. A. Naylor.)

corresponding mixtures should be as widely different as the thermal (or thermometric) conductivities; this is not so, for the speeds are nearly or quite equal. Hence, the formula of Mallard and Le Chatelier is incorrect, so far as the factor L is concerned.

The "Maximum Speed" Mixtures of Methane and Various "Atmospheres"

As the composition of a methane-air mixture is altered, the speed of uniform movement of flame therein attains its maximum value at a methane content of 9.5 to 10%. The mixture for complete combustion contains but 9.46%, the maximum speed mixture containing, therefore, a small excess of the combustible gas. This displacement has been ascribed by W. Payman[14] to the influence of mass action, an effect which would have its maximum value, if the reaction were trimolecular ($CH_4 + 2O_2$) when 33.3% of methane was present. If the reaction be, as it seems, dimolecular ($CH_4 + O_2 = CO + H_2 + H_2O$), then the maximum value for the mass-action effect can be shown to occur when 50% of methane is present (for methane-air mixtures).

The argon and helium curves of Fig. 1, as well as the results obtained in the 5cm. tube, show that even in atmospheres in which argon and helium take the place of the nitrogen of air, the maximum speed mixtures contain approximately the same proportion of methane.

The results of Fig. 2 show a similar effect. The "theoretical" mixture for complete combustion contains 6.70% of methane, while the maximum speed mixtures are definitely richer in the combustible gas. For the results of Fig. 3 the "theoretical" mixture contains 7.65% of methane, and the maximum speed mixtures are, again, somewhat richer.

It has been thought that the influence of mass action on the rate of reaction in methane-air mixtures would be overshadowed by the influence of the widely different temperatures of the flames of such mixtures as 9, 10 and 11% of methane in air. No alternative explanation is available, however, and Payman's argument is strengthened by the present results, dealing as they do with widely different flame temperatures, heat capacities and thermal conductivities. If, however, this explanation is correct, it implies that the temperature coefficient of the rate of combustion of methane is comparatively small at flame temperatures. There seems to be no other experimental evidence available at present, either for or against this rather important conclusion.

The writers wish to acknowledge the assistance of the late Ben E. Hess and of F. J. Hartwell, who conducted the experiments illustrated in Fig. 1.

[14] Payman [*J. Chem. Soc.*, **117**, 48 (1920)] also gives illustrations from other gas mixtures.

Summary and Conclusions

The speed of uniform movement of flame in mixtures of methane with air and with artificial "atmospheres" composed of 20.9% of oxygen, the remainder argon or helium, has been observed in tubes of various diameters, for upward, horizontal and downward propagation of flame. The results indicate that, in this case at least, the important factors which determine flame speeds are: (1) the heat developed in the flame and the heat capacities of burnt and unburnt mixture; (2) the rate of chemical reaction. The rate of transmission of energy from the flame, whether it be by conduction of heat or by some form of readily absorbed radiant energy, is so rapid that but little change in flame speed is observed when helium (of high thermal conductivity and low absorption for radiant energy) is replaced by argon (of low thermal conductivity and higher absorption for radiant energy), the inert gas being present to the extent of about three-fourths of the whole mixture.

Certain observations concerning the composition of the "maximum flame-speed mixtures" of methane in various "atmospheres" have led to the suggestion that the temperature coefficient of the rate of oxidation of methane is relatively small at flame temperatures.

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[CONTRIBUTION FROM THE BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE, AND THE SAFETY IN MINES RESEARCH BOARD, BRITISH MINES DEPARTMENT]

CHEMICAL ACTION IN THE ELECTRIC SPARK DISCHARGE. THE IGNITION OF METHANE[1]

BY H. F. COWARD[2] AND E. G. MEITER[3]

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Introduction

The nature and sequence of the chemical changes which occur during the ignition of an explosive gas mixture have received little investigation. It is known, however, that a stream of small, weak sparks from an induction coil will cause, not explosion, but a gradual combustion of an explosive mixture.[4]

Other aspects of spark ignition have received considerable attention in

[1] This is a joint report on one of a series of investigations to decrease accidents in mines, being conducted under the coöperation between the Bureau of Mines, United States Department of Commerce, and the Safety in Mines Research Board, British Mines Department. Published with the approval of the Director, United States Bureau of Mines.

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[3] Assistant physical chemist, Pittsburgh Experiment Station.

[4] An intimate study of the gradual reaction of electrolytic gas ($2H_2 + O_2$) at reduced pressures in the continuous discharge has recently been reported by G. I. Finch and L. G. Cowen [*Proc. Roy. Soc.*, 111A, 257 (1926)].