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IGNITION OF NATURAL GAS-AIR MIXTURES BY HEATED METAL BARS[1]

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This communication records certain observations, of general scientific interest, concerning the influence of catalytically active surfaces on the ignition temperature of gas mixtures. The work is preliminary to a technical study of the possibilities that heated metal may directly or indirectly initiate gas explosions in coal mines.

The experimental work was conducted by the junior writer in the Electrical Section of the Pittsburgh Experiment Station of the Bureau of Mines at the instigation and under the general supervision of L. C. Ilsley, electrical engineer.

Influence of Solids on the Ignition of Gases

It was long ago observed that the apparent ignition temperature of an explosive gas mixture was raised by increase of the area of a solid body exposed to it, as, for example, by packing the containing vessel with fragments of glazed porcelain.[4] This was ascribed to the retardation which the solid exerts on the self-heating of the gas mixture; for if the vessel and its contents are at the same temperature, self-heating of the gas by its own combustion is more difficult the more there is of solid material exposed to absorb the thermal energy of the combustion.

When, however, the solid has a marked catalytic action, this might be expected to reduce the ignition temperature; the ignition of a jet of cold hydrogen when it has streamed for a few moments over platinized asbestos apparently confirms this expectation. On the other hand, the experiments reported herein show that a powerfully catalytic surface has to be far hotter to ignite an explosive mixture of natural gas and air than has a surface of equal dimensions but of small catalytic action. Furthermore, those mixtures of natural gas and air which are most violently explosive require the highest temperatures for ignition by a heated bar of catalytically active metal (platinum).

The new observations are not in conflict with that of the ignition of hydrogen by platinized asbestos, for this solid has relatively little mass, in comparison with its surface area, and becomes red- or white-hot before

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[4] Hélier, *Ann. chim. phys.*, [7] **10**, 521 (1897).

the gas in its interstices ignites. The metal bars used in the present experiments have so great a heat capacity that their temperature is but little affected by combustion around them. They behave rather as thermostats, whereas the platinized asbestos rapidly rises in temperature, accumulating heat from the gas first burning by slow combustion and thereby increasing the rate of burning of gas arriving subsequently.

Experimental

Strips of metal were heated electrically in the center of a gas-tight, rectangular gallery of about 4.5 cu. ft. capacity. The dimensions of the metal strips or bars were varied in some of the tests, but for comparison between different metals a standard size of 4.25 inches long (between the terminal clamps), 0.50 inch wide and 0.040 inch thick was chosen. At the high temperatures required for ignition, a length of about an inch at the center of the bar was found to be uniformly heated. Its temperature was observed by means of a thermocouple peened into the bar, and careful tests showed that when the couple was properly inserted the alternating current used in heating the bar did not interfere with the thermocouple current.

The gallery was fitted with a large release valve of waxed paper which burst when an explosive mixture was ignited. It also contained a large fan, used to ensure homogeneity of the gas mixture, and a smaller fan which was used in some experiments on the influence of turbulence on ignition.

The explosive gas mixtures used were composed of natural gas and air. The composition of the former was fairly constant during the series of experiments and averaged 93.2% CH_4, 3.3% C_2H_6, 1.5% C_3H_8, 0.5% C_4H_{10}, etc., and 1.5% N_2. The gas admitted to the gallery was measured approximately by means of a standard wet-type gas meter. When the gas and air had been well mixed by the fan, a sample was withdrawn and analyzed by the thermal conductivity method. Either gas or air was then admitted as required until the desired mixture was obtained. Occasional checks on the accuracy of the gas analysis, by comparing the thermal conductivity results with those obtained by a combustion analysis, were satisfactory.

When the atmosphere in the gallery had been prepared, the bar was rapidly heated to a few degrees short of the temperature at which, according to previous trials, ignition might be expected. The rate of rise of temperature was then somewhat retarded and the potentiometer used in connection with the thermocouple was adjusted continuously for zero galvanometer reading until ignition took place. Practice enabled the investigator to raise the temperature of the bar to the ignition point with sufficient rapidity to avoid any sensible change in the composition of the gas mixture in the gallery, and yet not too rapidly for the temperature of ignition to be noted accurately. The gallery was large enough to provide latitude in the duration of the heating period, and constant results were obtained within a wide range of variation of rate of heating.

The choice of metals suitable for experiment is limited; the metal must have a high melting point and must not oxidize too rapidly at temperatures well above 1000°. On account of rapid oxidation and irregular scaling, iron failed to give reproducible results, although samples from several sources were tried. Certain steels, copper and Monel metal were more regular but melted at temperatures which restricted their utility. Stainless steel and a British steel of special composition, which resists oxidation at high temperatures, gave reproducible results. Platinum and nickel were found to be the most satisfactory materials for use in a long series of tests, and the latter was adopted as a standard of comparison.

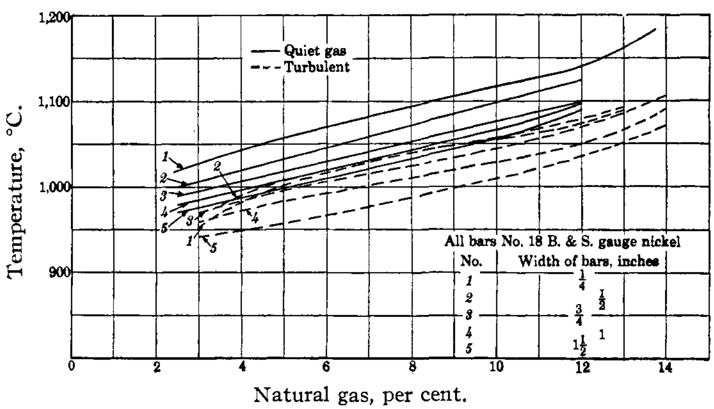

Fig. 1.—Ignition of natural gas and air mixtures by heated nickel bars.

The range in composition of the mixtures which are reported as "ignited" lies between 2.4 and 16% of natural gas. Ignition of mixtures near to the two limits was indicated by the sudden appearance of a cap of flame above the bar and an increase of pressure as shown on a manometer. It was only between the limits of 5.5 and 13.5% natural gas that the inflammation spread from the bar through most or all of the gas mixture.

Results of Experiments

1. Nickel Bars: Effect of Change of Bar Dimensions.—Nickel bars of various widths[5] were placed in the terminal clamps within the gallery in such a manner that their axes of length and thickness were horizontal, that is, they were on edge and the vertical dimension was varied. Fig. 1 shows the minimum temperatures at which the various bars ignited the

[5] These were cut from the same sheet of commercial nickel.

whole series of natural gas-air mixtures. The solid-line curves represent the results obtained when there was no mass movement of the gas other than that caused by convection currents about the heated bar. The broken curves represent results obtained in gas agitated by the rapid revolution of the small fan mounted several inches above the bar.

It is clear that the temperature necessary to ignite these mixtures by nickel bars increases with increase in natural-gas content of the mixture. No certain explanation for this is at present available.[6] The wider bars ignite the various mixtures more readily than the narrower bars; for the streaming gas is exposed for a longer period to the source of heat when in contact with the wider bars. Such turbulence as was imparted by the fan served to reduce the temperature necessary for ignition; but experiments now in progress show that when the turbulence is sufficiently great the opposite effect is produced.

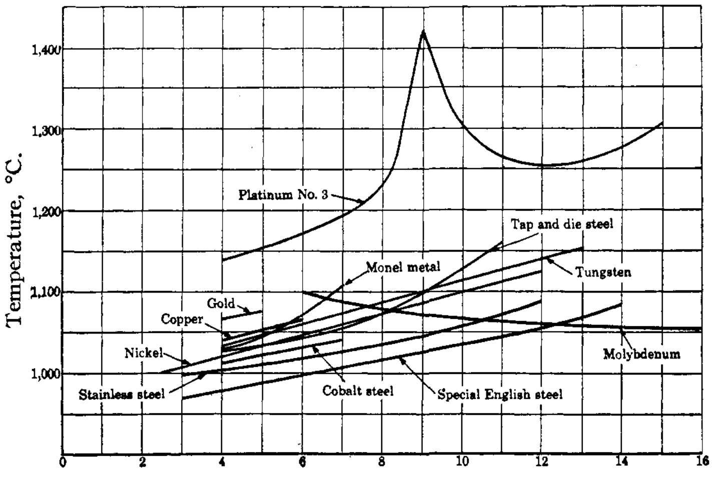

Fig. 2.—Ignition of natural gas mixtures by heated bars of various metals.

The limits of temperature at which ignition occurred with bars ranging between 0.25 and 1.5 inches in width, mixture composition between 2.5 and 14%, with and without turbulence, were 940 and 1180°. This range is widened by more extreme variations in the experimental conditions. For example, a thin nickel bar bent into the form of a slotted tube gave a value as low as 724°. The figures must, therefore, be regarded as relative, rather than absolute.

A few tests made with methane for comparative purposes showed that

[6] For a suggestion, made in connection with somewhat similar results observed in quartz vessels, see S. C. Lind, *J. Chem. Soc.*, **125**, 1867 (1924).

this gas, in contact with nickel, ignites at temperatures about 30° higher throughout the range of mixtures.

2. Effect of Different Metals on Ignition Temperatures.—Fig. 2 shows the minimum temperatures at which bars of various metals ignited the series of natural gas-air mixtures. As already stated, all the bars were of the same dimensions and were mounted as described in (1).

It appears (see also Fig. 3) that the various steels, copper, Monel metal and gold do not differ nearly so much in their ability to ignite the gas as the catalytically active metals platinum and palladium differ from nickel;

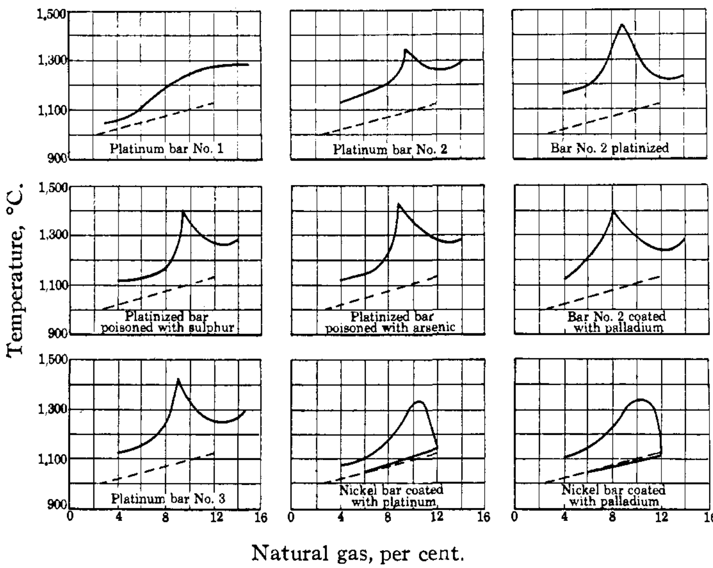

Fig. 3.—Ignition of natural gas-air mixtures by heated platinum and palladium surfaces. (The broken line in this figure represents the corresponding observations with a nickel bar.)

and three samples of platinum differed widely from one another. The abnormal character of the molybdenum curve is doubtless associated with the rapid burning of the metal; dense clouds of oxide were formed in all experiments. Tungsten did not give rise to an oxide cloud until raised to temperatures higher than any required for ignition of the gas mixtures.

Fig. 3 shows that while platinum sample No. 1 had to be much hotter than nickel in order to ignite the gas, the two curves are of similar type. Samples[7] No. 2 and 3, however, showed a remarkable peak in the neigh-

[7] We are indebted to the American Platinum Company for the following analysis of platinum bar No. 3: Pt, 99.51%; Ir, nil; Pd, 0.32%; Rh, 0.11%; Au, nil. The first bar had been remelted with other scrap metal before the desirability of an analysis was recognized.

borhood of the most violently explosive mixtures of gas and air, namely, those which contain just over 9% of natural gas.[8] Wüllner and Lehmann[9] record a similar result with a platinum wire of 0.5 mm. diameter suspended in methane-air mixtures. A stouter wire, also a platinum gauze, failed to show a maximum temperature for ignition in their other series of experiments.

Further experiments with platinum bar No. 2 showed that this effect could be increased by electrolytically depositing finely divided platinum or palladium upon the surface of the bar, and thereafter could be decreased somewhat by treating the bar with such catalytic poisons as arsenic and sulfur. These poisons burned off, however, after the first few ignitions and the characteristics previously showed by the bar were restored.

That the most explosive mixture should require the highest temperature for ignition by these two bars is evidence that the specific action of platinum is to be ascribed to its high catalytic activity in comparison with the weaker action of nickel and the other metals tested. In support of this contention is the variability of platinum bar No. 2 with chemical treatment and the dissimilarity of the curve for platinum bar No. 1. The consistency of the nickel results, in conjunction with the variability of the platinum results (as between the three samples), is what would be expected if platinum were the material subject to the vagaries of a catalyst and nickel were little more (in the case of natural gas and air) than a source of heat without much catalytic effect.

Further evidence in support of this view is also shown in Fig. 3. Two nickel bars were used, one coated with platinum and the other with palladium. Observations were made with increasing amounts of natural gas, and the upper parts of the two curves were obtained. In each case, after the observation with the 11% gas mixture, the subsequent figures (plotted in the lower part of the curve) followed closely the nickel curve. Doubtless the rare metal had dissolved and passed into the mass of the nickel when this occurred.

If it is correct to ascribe the high ignition temperature obtained with platinum to its high catalytic activity, direct evidence should be obtainable from an examination of the gases exposed to the hot metals. Parallel experiments were therefore made in which nickel and platinum bars were separately placed in mixtures containing 9% of natural gas and carefully maintained at 1050° for periods of 8 and 20 minutes. The results of the analyses of samples then taken after thoroughly mixing the gallery atmosphere with the fan were as follows.

[8] The "theoretical" mixture of natural gas and air, which has just sufficient oxygen to burn the gas completely, contains 9.09% of natural gas. Flame is propagated most rapidly in mixtures which are slightly richer than this. See ref. 11.

[9] Wüllner and Lehmann, "Anlagen zum Hauptbericht der Preussischen Schlagwetter Commission," **1886**, p. 219.

Combustion of Gases during Pre-flame Period

Gas present	With platinum bar, %	With nickel bar, %
Natural gas, at start	9.1	8.99
CO_2, after 8 minutes	1.01	0.05
CO, after 8 minutes	0.72	.50
Natural gas, at start	8.75	8.77
CO_2, after 20 minutes	1.96	0.07
CO, after 20 minutes	0.22	.36

It will be seen that more than 20 times as much carbon dioxide was formed with the platinum bar as was formed with the nickel at the same temperature.

In all the higher percentage mixtures employed, when the mixture was not inflamed, quiet combustion around the platinum maintained its temperature above red heat for several minutes after the heating current had been shut off. This was not observed at any time with the nickel bar and is further evidence, if any were needed, of the superior catalytic action of platinum at high temperatures on natural gas-air mixtures.

3. Comparative Experiments with Nickel and Quartz.—It is generally accepted that fused quartz has relatively little catalytic action on the combustion of the paraffin hydrocarbons.[10] If, then, nickel and fused quartz should give similar results in similar circumstances, it might be concluded that nickel also had little catalytic action on the combustion of natural gas. As it was not possible to heat a quartz bar by the same means as the metal bars had been heated, a comparison of the ignition temperatures in tubes was adopted. The ignition temperature of natural gas in a certain quartz tube was about 620° and varied but little over the whole range of inflammable mixture.[11]

Tubular vessels of length and diameter equal to the quartz tube were made from two samples of nickel sheet and were heated by the same means as had been used for the metal bars in the same chamber. A narrow slit was left along the bottom of each tube and when ignition occurred within, flame was seen to be projected through the slit and to ignite the main mass of gas outside. In these circumstances the range of ignition temperatures for mixtures containing from 4 to 12% of natural gas was 832 to 878° in one tube, 724 to 800° in another. It had been expected that much lower ignition temperatures would be obtained for the nickel tubes than for the nickel bars, for Mallard and Le Chatelier[12] had found that methane was ignited by a heated iron crucible at a much lower temperature when the gas was allowed to stream up into the in-

[10] See, for example, H. B. Dixon and H. F. Coward, *J. Chem. Soc.*, **95**, 514 (1909). W. Mason and R. V. Wheeler, *ibid.*, **121**, 2079 (1922); **125**, 1869 (1924).

[11] Coward, Jones, Dunkle and Hess, Bull. 30, Carnegie Inst. of Tech., "The Explosibility of Methane and Natural Gas," **1926**, 42 pp.

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

verted crucible than when the gas streamed up around the outer surface of the crucible in its normal position. This they explained on the basis of the effect of convection currents in removing hot gases before the end of the "time lag" prior to inflammation. The figures obtained with the two tubes used in the present experiments differed somewhat widely; the difference may be due to some difference in shape or in material, although bars cut from the two samples of nickel sheet gave almost identical figures. However that may be, it is clear that in a comparison between quartz and nickel surfaces, the quartz surface of small catalytic action gives the lower ignition temperature. In view of this, and in the light of the conclusions drawn regarding the high catalytic action of platinum, it must be concluded that nickel itself has a significant catalytic action on the combustion of natural gas.

The most probable explanation of the apparent paradox (that catalytic action of a solid surface tends to raise the ignition temperature of a gaseous mixture) can hardly be given better than in the words of Mason and Wheeler.[10]

"The mixture immediately surrounding the heated surface may be consumed so rapidly as to become incapable of propagating flame, the reaction continuing to take place only at or near the heated surface even though its temperature there may rise far above the true ignition temperature of the mixture."

The effect of moderate turbulence must be to bring inflammable gas into the zone of burnt-out mixture, and thus to raise its temperature, perhaps to the ignition point, when it is near but not on the heated surface.

Summary

Measurements of the temperatures at which metal bars ignite mixtures of natural gas and air show that:

1. In parallel experiments the metals of greater catalytic effect must be hotter to cause ignition than metals or other substances of smaller catalytic effect. The difference may be several hundred degrees.

2. The temperature necessary to ignite these mixtures by bars of nickel, tungsten and several special steels increased regularly with increase in natural gas content throughout the whole range of inflammable mixtures.

3. With two of the three platinum bars tested, a much higher temperature was required to ignite the most violently explosive mixtures than was required to ignite mixtures of less explosibility.

A record is also given of the effect of variations in dimensions of the heated bar and of the effect of moderate turbulence on the ignition of these gaseous mixtures.

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