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THE FLAME TEMPERATURES OF MIXTURES OF AMMONIA AND ITS PRODUCTS OF DISSOCIATION¹

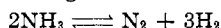
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The United States Bureau of Mines has received many inquiries relative to the flame temperature of ammonia and its products of dissociation. Ammonia can now be manufactured rather cheaply and is being produced in such quantities that there are difficulties in finding an adequate market. The gas can be compressed in the liquid form in cylinders, and if it can be burned directly with air, or, if necessary, partially or completely cracked at the place where it is used, it may become of industrial importance as a heating, welding or cutting gas.

Ammonia decomposes according to the following reaction



Completely "cracked" ammonia therefore consists of a mixture containing 75% of hydrogen and 25% of nitrogen.

The method of determining the flame temperatures was the same as described in previous publications,^{5a,b,c} with certain modifications (described later) when ammonia was one of the constituents.

The Flame Temperature of Hydrogen-Nitrogen-Air Mixtures.—The flame temperatures of hydrogen-air mixtures have been measured^{6c} and the maximum temperature was found to be 2045°. The flame temperatures of hydrogen-nitrogen-air mixtures were measured to determine the effect of adding nitrogen to the hydrogen-air mixtures. The results are shown graphically in Fig. 1. A mixture containing three volumes of hydrogen and one of nitrogen (representing completely cracked ammonia) has a maximum flame temperature of 1885°. The addition of this amount of nitrogen has therefore reduced the flame temperature about 160°. Incidentally, this temperature is approximately the same as the maximum flame temperature of methane or Pittsburgh natural gas in air.

Further additions of nitrogen depress the maximum flame temperature still more. For nitrogen and hydrogen in equivalent amounts it is 1680°.

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⁵ (a) Loomis and Perrott, *Ind. Eng. Chem.*, **20**, 1004 (1928); (b) Jones, Lewis, Friauf and Perrott, *THIS JOURNAL*, **53**, 869 (1931); (c) Jones, Lewis and Seaman, *ibid.*, **53**, 3992 (1931).

whereas when approximately two volumes of nitrogen are present to one of hydrogen it has dropped to 1465° .

These results are of interest in showing the marked effect that inert gases such as nitrogen have on the maximum flame temperature of combustibles when burned with air and emphatically suggest the importance of keeping inerts in manufactured gas and other industrial gaseous fuels to a minimum if a maximum flame temperature is desired.

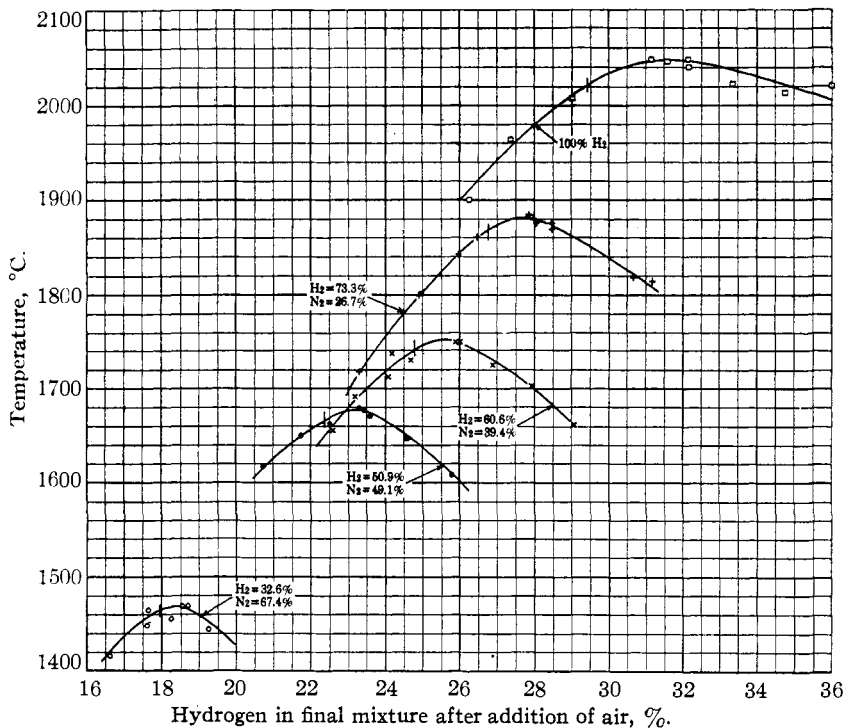


Fig. 1.—Flame temperatures H_2 - N_2 -air mixtures.

In the curves shown in Fig. 1, the percentages of hydrogen present representing complete combustion are indicated by short vertical lines crossing the curves. In agreement with results previously obtained for other combustibles,^{5a,b,c} the maximum temperatures occur slightly on the rich side.

Figure 2 shows graphically the decrease in the maximum flame temperature with increase in nitrogen content. The decrease is almost directly proportional to the percentage of nitrogen in the original hydrogen-nitrogen mixture before the addition of air. It was found impossible to obtain flame temperatures, by the method used, when more than about two volumes of nitrogen was present for one volume of hydrogen, because

the reversal of the sodium line was too indistinct. Determinations with larger proportions of nitrogen were abandoned.

The Flame Temperatures of Ammonia-($3\text{H}_2 + \text{N}_2$)-Air Mixtures.—It was found impossible to burn straight ammonia in air (in order to obtain its flame temperature) at laboratory temperature with the various burners tried. The rate of flame propagation is too small to prevent the flame from blowing off the burner ports. Determinations were made with mixtures of ammonia and its dissociation products ($3\text{H}_2 + \text{N}_2$). An extrapolation for the maximum flame temperature of pure ammonia might then be made from these data.

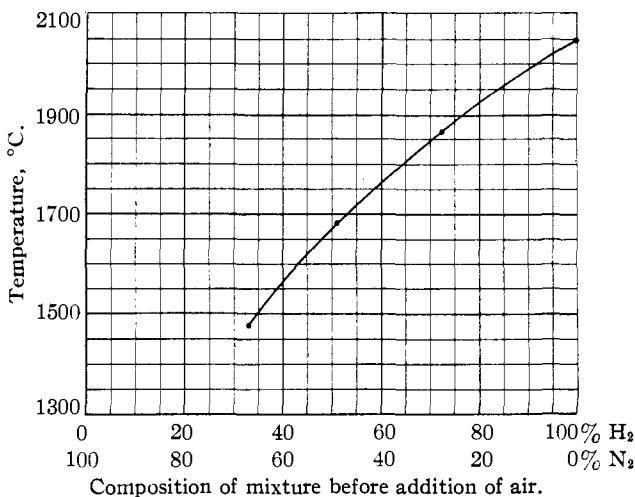


Fig. 2.—Maximum flame temperatures H_2 - N_2 -air mixtures, determined values.

Since ammonia is very soluble in water and glycerin-water mixtures the procedure for preparation of the gas mixtures had to be altered. They were prepared and stored in a high-pressure cylinder. Ammonia, nitrogen and hydrogen under high pressure (in tanks) were measured into an empty cylinder by means of a calibrated pressure gage in desired amounts. The gases were mixed by tilting the cylinder and applying gentle heat on one side near the bottom. Due to the convection currents set up, it was found that one hour was sufficient to mix the gases thoroughly. Samples of gas were then withdrawn for analysis. One sample was stored over dilute acid solution to absorb the ammonia. The unabsorbed gases, hydrogen and nitrogen were then transferred to a Bone and Wheeler gas analysis apparatus and determinations made for hydrogen, oxygen and nitrogen (the latter by difference). The percentage of oxygen present in the sample was assumed to be due to contamination by air. Correction for the amount of nitrogen associated with oxygen in air was made. If the ratio

of hydrogen to nitrogen was not three to one, more of one of the gases was added and the analysis repeated. For the analysis of ammonia the gas was passed into a 240-cc. calibrated sample tube and the sample taken over clean dry mercury. The temperature and pressure were recorded. The gas sample was passed through two efficient absorption bulbs (Bowen type) containing $N/10$ sulfuric acid. The unneutralized acid was titrated back with standard ammonium hydroxide solution using a cochineal indicator. The percentage of ammonia could then be calculated. Knowing the ammonia content the percentage of hydrogen and nitrogen in the original mixture could then be evaluated.

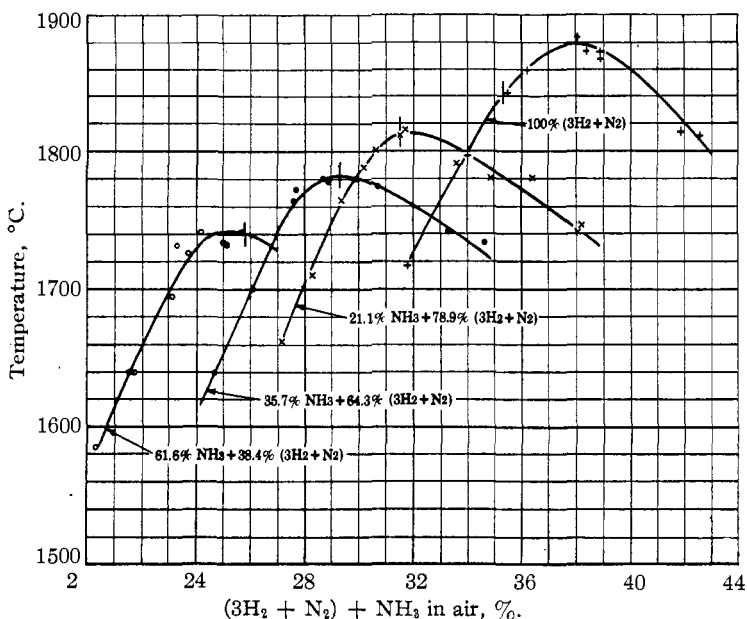


Fig. 3.—Flame temperature of mixtures of ammonia and its products of dissociation in air.

The flame temperatures of mixtures of ammonia and its dissociation products are shown in Fig. 3. The maximum flame temperature decreases with increasing proportions of ammonia. For 61.6% ammonia in the original combustible mixture it is 1740°. It was impossible to determine flame temperatures on the rich side of this mixture because the flames elongated and blew off the burner ports. Determinations for mixtures containing more than 61.6% ammonia were discontinued. The maximum flame temperatures occur slightly on the rich side except for the mixture containing the highest proportion of ammonia.

The maximum flame temperatures are plotted in Fig. 4. It is of interest to compare these with the maximum flame temperatures of the mixtures

calculated by the method described elsewhere^{5b} and represented by the upper curve in Fig. 4. They are about 75° higher than the observed, which is attributable to radiation losses. This difference is constant over the range investigated. The calculated maximum flame temperature for ammonia-air mixtures is 1775° . On this basis, assuming the difference to hold throughout the entire range, the observed maximum flame temperature of ammonia-air mixtures, if a laboratory burner could be developed to burn them, would be about 1700° .

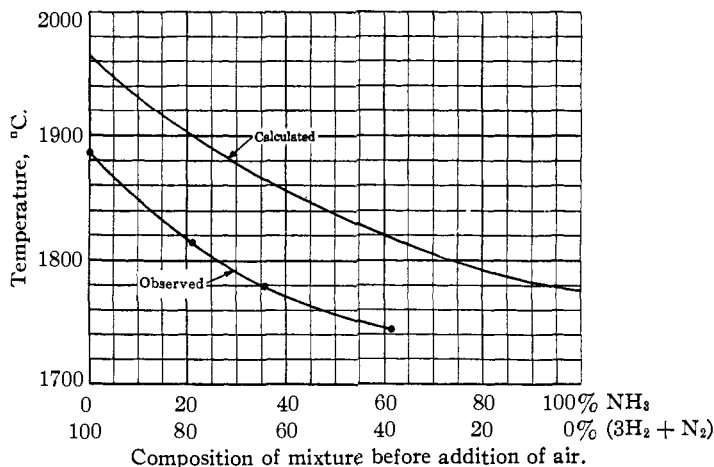


Fig. 4.—Maximum flame temperatures of ammonia-($3\text{H}_2 + \text{N}_2$)-air mixtures.

Summary

The flame temperatures of hydrogen-nitrogen-air mixtures and ammonia-($3\text{H}_2 + \text{N}_2$)-air mixtures have been measured by the sodium line reversal method.

The maximum flame temperature of a mixture $3\text{H}_2 + \text{N}_2$ is 1885° —about the same as that found for methane or Pittsburgh natural gas burning in air. Temperatures for other proportions of hydrogen and nitrogen are given.

The maximum flame temperature of ammonia, as determined by extrapolation, is 1700° .

The flame temperatures have been calculated and are in good agreement with the observed values.

PITTSBURGH, PENNSYLVANIA