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UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
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FLAMMABILITY OF HYDROGEN-AIR-NITROGEN OXIDE MIXTURES

Final Report

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ABSTRACT

Limit-of-flammability tests were conducted on various hydrogen-air-nitric oxide-nitrous oxide mixtures at one atmosphere pressure and ca. 28°C. The data used to define the limits of flammability of the above mixtures are presented in tabular and graphic form and are used to construct a flammable volume in a regular tetrahedron in which the apices are pure H_2 , air, NO and N_2O .

Le Chatelier's law (mixture law) was found to be obeyed only by upper and lower limit mixtures of hydrogen, air and nitrous oxide and by lower limit mixtures of hydrogen, nitric oxide and nitrous oxide. The deviations from this law are greatest for upper limit mixtures of hydrogen, air and nitric oxide. The minimum in this upper limit curve occurs at the nitric oxide-air mixture composition which contains two volumes nitric oxide per volume oxygen.

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1. INTRODUCTION

The tests conducted by the Bureau of Mines under Atomic Energy Commission Appropriation 14-899/60101(09) were part of an investigation of the potential gas explosion hazards in a chemical processing plant operated by the Phillips Petroleum Company (see letter of September 2, 1955 to Mr. J. Bion Philipson, U. S. Atomic Energy Commission from Dr. Robert W. Van Dolah, Bureau of Mines).

The results of flammability tests conducted on various hydrogen-air-nitrogen oxide mixtures, procedures used to conduct these tests, and a discussion of the results are given below.

2. EXPERIMENTAL WORK AND DISCUSSION

Limit-of-flammability tests were conducted on various hydrogen-air-nitric oxide-nitrous oxide mixtures at one atmosphere pressure and ca. 28°C. in the standard Bureau of Mines apparatus (see Bureau of Mines Bulletin 503, "Limits of Flammability of Gases and Vapors" by H. F. Coward and G. W. Jones, 1952). Two procedures were used to conduct these tests. The procedure outlined in Bulletin 503 was used for all tests involving nonreacting gas mixtures at room temperature, otherwise the mercury mixer was not used and mixing was achieved by diffusion. Adequacy of mixing was evaluated for a number of mixtures by determining the limits of flammability when the mixture components were added in various sequences. In addition, from previous work it is known that an inadequately mixed limit test mixture is characterized by a nonuniform flame movement through the glass explosion chamber of the test apparatus.

Gas compositions were calculated from the partial pressures of the n mixture components in the case of initially nonreacting mixtures and from $n-1$ partial pressures plus the final pressure in the case of the reacting mixtures. In short, for nonreacting mixtures such as H_2 -air- N_2O , the mixture composition is

$$\% i = \frac{100 p_i}{\sum_{j=1}^n p_j} = \frac{100 p_i}{P} \quad (1)$$

where $\% i$ is the concentration of the i^{th} component in the test mixture, p_i is the partial pressure of the i^{th} component and $P (\sum_{j=1}^n p_j)$ is the total system pressure (equal to one atmosphere in this study) for the n -component mixture. However, for reacting mixtures such as H_2 -air- NO , $P \neq \sum_{j=1}^n p_j$, since the oxygen in the air and the nitric oxide react to give a mixture of

NO_2 and N_2O_4 ; the exact mixture composition at one atmosphere pressure depends on the temperature. This, of course, poses a problem as to the most useful method of representing the data obtained in these limit-of-flammability tests. A mixture composition that is based on the gases present after the initial reaction has occurred would be temperature dependent, since the extent of dissociation of the N_2O_4 formed from NO and oxygen is temperature dependent. On the other hand, the mixture composition would be fixed if it were based on the gases present before reaction occurs. To calculate mixture compositions in this case from $n-1$ partial pressure measurements and one final pressure, one must know the equilibrium composition for an NO_2 - N_2O_4 mixture at the test temperature, since this will affect the final pressure, P . The equilibrium composition was taken as 35 percent NO_2 , 65 percent N_2O_4 . Mixture compositions were obtained by using the measured partial pressures for hydrogen, NO_2 and NO and the calculated partial pressure for air using the equation

$$\% \text{ A} = \frac{100 P_A}{\sum_{j=1}^n P_j} \quad (2)$$

The partial pressure of the air (y) put into the mixture was calculated with the following equations (see Appendix),

$$y = 1.601 (P-w-x-z) \quad , \quad z \geq 0.42 y \quad (3)$$

$$y = P-w-x-0.1061z \quad , \quad z \leq 0.42 y \quad (4)$$

where

P = final pressure after reaction
 w = partial pressure of N_2O
 x = partial pressure of H_2
 z = partial pressure of NO.

Equations (3) and (4) are needed to take care of compositions in which an excess of NO or O_2 exists respectively.

The data used to define the limits of flammability of the various mixtures tested are given in tables 1-6 and presented graphically in figures 1-6. These figures are sections of a flammable volume in a regular tetrahedron in which the apices are pure H_2 , air, NO and N_2O . Such a composite figure is given in figure 7.

All test data not listed in tables 1-6 fall in two categories, the first are flammable mixtures with mixture compositions within the flammable range and the second are nonflammable mixtures with mixture compositions outside the flammable range. These latter mixtures, as well as those listed as nonflammable in tables 1-6, do propagate flame for a

short distance up the explosion chamber, since the ignition source elevates the temperature of the surrounding gases thus widening the limits of flammability in the immediate vicinity of the spark electrodes. However, the flame propagates only a short distance and dies out before the chamber pressure is affected appreciably.

Reliable published limit-of-flammability data on the system under consideration are included in tables 1-6 and in figures 1-6. The agreement between the data obtained in this investigation and the existent reliable data is quite good.

The broken lines in figures 1-6 are the limits of flammability based on Le Chatelier's law (mixture law) which states that a homogeneous mixture of limit mixtures is itself a limit mixture. This law is obeyed only by upper and lower limit mixtures of hydrogen, air and nitrous oxide and by lower limit mixtures of hydrogen, nitric oxide and nitrous oxide. The deviations from the law are greatest for mixtures of hydrogen, air and nitric oxide. This deviation is, of course, accentuated for upper limit mixtures but reduced for lower limit mixtures because of the method used in calculating these limits (see Appendix). It is interesting to note that the shapes of the upper and lower limits for mixtures of hydrogen, air and nitric oxide (figure 3) are similar to those for mixtures of hydrogen, air and bromine (see R. F. Simmons and H. G. Wolfhard, "The Influence of Methyl Bromide on Flames," Trans. Faraday Soc., Vol. 51, Part 9, September 1955, page 1214). The minimum in the upper limit curve for the hydrogen, air, nitric oxide mixtures occurs at the nitric oxide-air mixture composition which contains two volumes nitric oxide per volume oxygen, whereas the maximum in the lower limit occurs at a mixture composition which is richer in nitric oxide.

In addition to the above limits, the lower limit of flammability was determined for hydrogen in a stoichiometric nitric oxide-oxygen mixture, that is, a mixture made up of two volumes nitric oxide and one volume oxygen. This limit (7.5 percent H_2) is the same as that in a nitric oxide-air mixture which contains two volumes nitric oxide per volume oxygen. This is rather surprising in view of the fact that the specific heats of NO_2 and N_2O_4 , which are in excess in the first mixture, are higher than that of nitrogen, which is in excess in the second mixture.

One further point checked during this investigation was the possibility of the heat of the nitric oxide-oxygen reaction initiating the hydrogen-oxygen reaction. A gas burette was used to add measured volumes of hydrogen, air and nitric oxide to an evacuated glass apparatus. A mercury manometer was used to measure the pressure after each volume of gas was added to the glass apparatus. The final system pressure checked the pressure that was calculated on the assumption that only nitrogen dioxide and nitrogen tetroxide were formed; therefore, water must not have been formed.

APPENDIX

Reacting Gas Mixture Composition Calculations.

In making up a gas mixture in which two or more reacting components are used, Dalton's law of partial pressures may not be obeyed so that the total pressure P is not equal to the sum of the partial pressures. Consider, for example, a hydrogen-nitrous oxide-nitric oxide-air mixture in which each component is added to a constant volume system so that partial pressure measurements are made on each component except air; as the air is added, the oxygen and nitric oxide react to produce NO_2 and N_2O_4 so the quantity of air added must be calculated from the final pressure. This is then used to formally calculate the mixture composition on the assumption that Dalton's law is obeyed. A similar treatment using the Amagat-Leduc law of partial volumes could be used; however, in general, it would not be as precise for a system with as large a volume as the partial pressure method.

As noted above, the NO_2 and N_2O_4 produced when air is added to NO must be known to calculate the partial pressure of air added to the system $\text{H}_2\text{-N}_2\text{O-NO}$ from the final pressure. The equilibrium between NO_2 and N_2O_4 is temperature and pressure dependent; however, at one atmosphere pressure the equilibrium concentration can be expressed in terms of a dissociation constant, α , which represents the fraction of the original N_2O_4 that dissociates. For example, at ca. 28°C . and one atmosphere pressure, one mole N_2O_4 would yield an equilibrium mixture of 2α or 0.42 mole NO_2 and $(1-\alpha)$ or 0.79 mole N_2O_4 ; i.e. 35 percent NO_2 , 65 percent N_2O_4 . Under these conditions, a mixture of x^0 moles H_2 , w^0 moles N_2O , y^0 moles air and z^0 moles NO would give:

Then, assuming Dalton's law of partial pressures is obeyed, the above equations give:

$$y = 1.60(P - w - x - z) \quad , \quad z \geq 0.42y \quad (3)$$

$$y = P - w - x - 0.105z \quad , \quad z \leq 0.42y \quad (4)$$

where w , x , y and z are the partial pressures of NO_2 , H_2 , air and NO , respectively, and P is the final pressure after the gases are mixed. Knowing the partial pressures w , x , y and z (or p_1 , p_2 , p_3 and p_4 , respectively),

a mixture composition can be defined so that

$$\% i = \frac{100 p_i}{\sum_{j=1}^4 p_j} \quad (7)$$

as in the case of the nonreacting gas mixtures (Eq. 1), the only difference being that here $\sum_{j=1}^4 p_j \neq P$. If the total pressure P were used instead of the summation in Eq. 7 above, the percentages of the nonreacting constituents would be increased by the ratio $\frac{1}{P} \cdot \sum_{j=1}^4 p_j$; that is, the lower and upper limits would be increased.

Table 1. - Limits-of-flammability data for hydrogen-nitric
oxido-nitrous oxide mixtures at ca. 28°C. and one
atmosphere pressure.

Test No.	Composition (mole %)			Propagated flame?
	H ₂	NO	N ₂ O	
(LOWER LIMIT)				
7	5.7	93.3	---	Yes
8	6.5	93.4	---	No
59	5.3	47.4	47.3	Yes
54	5.0	47.5	47.5	No
198	5.5	54.5	40.0	Yes
18	3.0	---	97.0	No
20	3.4	---	96.9	Yes
(UPPER LIMIT)				
17	66.0	34.0	---	Yes
16	66.9	33.1	---	No
50	67.5	25.5	7.0	No
48	67.0	25.0	8.0	Yes
39	68.4	15.8	15.8	Yes
36	68.7	15.7	15.6	No
51	72.3	10.0	17.2	No
52	71.9	10.5	17.6	Yes
40	77.9	5.5	16.6	No
42	78.2	4.5	17.4	Yes
197	68.0	16.0	16.0	Yes
25	84.6	---	15.4	No
22	83.7	---	16.3	Yes

Table 1. - Limits-of-Flammability data for hydrogen-nitrous oxide-air mixtures at ca. 25°C. and one atmosphere pressure.

Test No.	Composition (mole %)			Propagated flame?
	H ₂	N ₂ O	Air	
(LOWER LIMIT)				
18	3.0	77.0	—	No
20	3.1	96.9	—	Yes
— a/	4.0	—	96.0	Limit mixture
47	3.9	48.1	48.0	Yes
44	3.5	48.2	48.3	No
195	4.9	25.0	70.5	Yes
(UPPER LIMIT)				
25	84.6	35.4	—	No
22	83.7	16.3	—	Yes
— a/	75.0	—	25.0	Limit mixture
191	81.0	9.5	9.5	Yes
— b/	83.4	10.3	3.3	Limit mixture
— b/	82.1	10.7	7.2	Limit mixture
— b/	80.0	3.0	13.0	Limit mixture
— b/	77.4	4.5	18.1	Limit mixture

a/ Coward, H. P. and Jones, G. W., Limits of Flammability of Gases and Vapors, Bureau of Mines Bulletin 503, 1952, p. 130.

b/ Smith, S. and Linnett, J. W., The Upper Limits of Inflammability of Hydrogen-Air and Hydrogen-Nitrous Oxide Mixtures, Jour. Chem. Soc. (London), 1953, pp. 37-45.

Table 3. - Limits-of-flammability data for hydrogen-nitric oxide-air mixtures at ca. 28°C. and one atmosphere pressure.

Test No.	Composition (mole %)			Propagated flame?
	H ₂	NO	Air	
(LOWER LIMIT)				
104	6.8	9.3	85.9	Yes
103	5.3	13.2	81.5	No
101	7.1	24.8	68.1	No
102	7.5	24.6	67.9	Yes
108	14.2	41.7	44.1	No
89	14.8	35.3	49.9	No
109	15.6	36.8	47.6	No
114	16.0	42.2	41.8	Yes
88	16.2	38.1	45.7	Yes
110	17.3	35.4	47.3	Yes
113	8.3	71.2	20.5	No
111	10.8	63.3	25.9	Yes
(UPPER LIMIT)				
150	69.8	2.0	28.2	No
149	64.9	2.0	33.1	Yes
138	57.5	4.8	37.7	No
187	57.1	3.7	39.2	Yes
139	46.7	7.4	45.9	Yes
154	46.0	9.2	44.9	No
153	43.1	9.2	47.7	Yes
152	39.1	12.5	48.4	No
140	33.9	17.0	49.1	Yes
146	31.1	20.4	48.5	Yes
145	32.2	21.4	46.4	No
144	32.0	26.1	41.9	Yes
147	36.1	25.7	38.2	No
186	34.4	27.9	37.7	Yes
151	44.9	27.8	27.3	No
143	51.2	30.8	18.0	Yes
147	57.2	30.5	12.3	Yes
155	62.2	30.1	7.7	No
193	63.0	32.4	4.6	Yes

Table 4. - Limits-of-flammability data for hydrogen-nitric oxide-nitrous oxide-air mixtures at ca. 28°C. and one atmosphere pressure. (% NO/% N₂O = 0.257).

Test No.	Composition (mole %)				Propagated flame?
	H ₂	NO	N ₂ O	Air	
		(LOWER LIMIT)			
185	6.2	66.4	25.9	1.5	Yes
184	6.4	64.1	24.9	4.6	Yes
183	5.9	63.3	24.6	6.2	No
122	6.4	51.7	20.2	21.7	Yes
118	6.1	42.8	16.6	34.5	No
120	7.2	28.9	11.3	52.6	Yes
121	5.5	24.3	9.4	60.8	No
119	6.6	19.1	7.5	66.8	Yes
123	4.3	15.6	6.0	74.1	No

Table 5. - Limits-of-Flammability data for hydrogen-nitric oxide-nitrous oxide mixtures at ca. 23°C. and one atmosphere pressure. (% NO/% H₂O = 1.0)

Test No.	Composition (mole %)				Propagated flame?
	H ₂	NO	H ₂ O	Air	
(LOWER LIMIT)					
150	1.0	7.3	7.3	61.0	No
131	6.3	12.4	12.4	63.9	Yes
126	6.9	15.9	15.9	61.3	Yes
124	1.7	13.0	13.0	57.1	No
127	7.0	19.1	19.1	54.2	Yes
128	5.1	27.2	27.1	49.6	No
129	6.3	31.5	32.5	28.7	Yes
(UPPER LIMIT)					
160	59.5	1.0	1.0	23.5	Yes
159	70.1	1.5	1.5	26.9	No
156	51.3	4.3	4.8	30.6	Yes
200	61.3	4.3	4.8	27.1	No
176	52.9	5.2	9.2	23.7	Yes
174	55.0	9.2	9.2	23.3	No
178	52.9	10.0	10.0	27.1	No
177	57.1	10.8	10.0	25.3	Yes
180	59.0	12.0	13.8	13.4	No
181	59.3	14.7	14.3	12.0	Yes
168	66.2	15.0	15.3	3.2	No
182	66.1	15.9	15.9	2.1	Yes

Table 6. - Limits-of-flammability data for hydrogen-nitric oxide-nitrous oxide-air mixtures at ca. 28°C. and one atmosphere pressure. ($\% \text{ NO} / \% \text{ N}_2\text{O} = 0.33$).

Test No.	Composition (mole %)				Propagated flame?
	H ₂	NO	N ₂ O	Air	
		(LOWER LIMIT)			
136	5.3	15.3	45.9	33.5	Yes
135	4.5	12.5	37.3	45.7	No
132	6.3	10.9	32.5	50.3	Yes
133	4.5	10.9	32.6	52.0	No
134	5.6	8.7	26.3	59.4	Yes
137	4.1	8.4	25.0	62.5	No

12

100 0

LEGEND

- O - Flammable mixture
X - Nonflammable mixture

Figure 1. - Limits of flammability of the system H_2 -NO- N_2O at ca. 28°C. and one atmosphere pressure.

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LEGEND

- O - Flammable mixture
- X - Nonflammable mixture
- ▲ - Coward and Jones,
Bureau of Mines
Bull. 503.

Figure 3. - Limits of flammability of the system H_2 -NO-Air at ca. 28°C. and one atmosphere pressure.

LEGEND

- O - Flammable mixture
- X - Nonflammable mixture
- ▲ - Coward and Jones, Bureau of Mines Bull. 503.
- - Limit value from figure 1.

Figure 4. - Limits of flammability of the system H_2 -NO- N_2O -Air at ca. $28^\circ C$. and one atmosphere pressure.
(% NO/% N_2O = 0.257)

Figure 7. - Limits of flammability of the system H_2 -NO- N_2O -air at one atmosphere pressure and ca 28° C.