

Oxides of Nitrogen in Combustion

Effects of Pressure Perturbations

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Experimental information was obtained concerning the residual quantities of the oxides of nitrogen under conditions of oscillatory combustion. Results indicated a marked variation in behavior with change in mixture ratio. The frequency of the oscillations shifted significantly from one regime to another in the vicinity of a stoichiometric mixture ratio. The quantities of oxides of nitrogen changed from 2 to more than 60×10^{-6} mole fraction with a change in mixture ratio.

THE PRESENCE of nitrogen oxides in the reaction products of industrial fuels has become a problem of increasing importance from the standpoint of air pollution (1). Since a number of eye irritants and other undesirable compounds in the atmosphere originate with the oxides of nitrogen (2, 3, 4, 5, 6), an understanding of the factors contributing to their formation seems worthwhile.

Early reconnaissance studies (7, 8) indicated that perturbations in pressure at frequencies from 400 to 1000 cycles per second contributed materially to the quantities of the oxides of nitrogen which remain in the products of combustion of air and natural gas. More recently, Richter and co-workers (1) indicated the marked effect of perturbation frequency upon the formation of the oxides of nitrogen, and the frequency appears to be a function, perhaps discontinuous, of the mixture ratio of air and natural gas. Richter (1) established need for careful control of combustion conditions if pseudo-steady conditions in regard to oscillatory combustion were to be maintained. As would be expected, increase in the frequency of perturbations increased the change in pressure across the combustion zone. Furthermore, variation in the double amplitude of the pressure changes during oscillatory combustion was found to be much greater than the changes in frequency under conditions encountered with the experimental equipment used by Richter (1).

The present investigation covers in greater detail the same type of experimental measurements as carried out by Richter, with emphasis upon behavior at a reactant velocity of approximately eight feet per second in a premixed flame of air and natural gas.

EXPERIMENTAL METHODS

The apparatus used in this study has been described (1, 8). In principle, it consists of a water-cooled vertical combustor constructed of a copper tube approximately four inches in diameter and 13 feet in length. A mixture of air and natural gas of appropriate composition was introduced into the lower part of the combustor, passed through a perforated-plate flame holder, ignited by a spark above the flame holder and vented through an acoustic silencer located at the exit of the combustor. Sampling ports were provided along the walls of the combustor. In this investigation all

samples of the products of reaction were taken approximately 100 inches above the flame holder. The pressure transducer, with a response of approximately 10 kilocycles and a sensitivity of 0.01 pound per square inch, is located at a distance approximately 16 inches above the flame holder. A four-vane baffle was located immediately above the perforated copper-plate flame holder. This four-vane baffle, constructed of welded stainless steel, permitted measurements at higher and lower mixture ratios than was possible without the baffle.

Air was supplied from a pair of centrifugal blowers driven by a direct-current motor whose speed was controlled by a quartz oscillator (9). The rates of flow of the air and the natural gas were determined by means of Venturi meters whose design complied with existing standards (10). The flow rates of the air and natural gas were each known within approximately 0.5 per cent. Air-water and gas-water manometers were used to determine the differences in static head between the upstream and the throat of the Venturi meters. The temperatures of air and cooling water were determined with an uncertainty of 0.1° F. Specific weight of the natural gas was measured on a semi-continuous basis and composition was determined periodically. Variation in specific weight found during the course of a single measurement was not sufficiently large to introduce measureable uncertainties in the composition of the products of reaction.

The desired flow rates of air and of natural gas were established, the mixture ignited above the flame holder, and a quasi-steady state attained. This required a period of at least 1000 seconds. Quadruplicate samples were then obtained for determining the oxides of nitrogen. Concentrations of the latter molecular species were determined by the phenol-disulfonic acid method (11). With each sample-taking a series of three measurements of pressure perturbations was obtained with the condenser-type transducer described earlier (1). A typical set of oscillograph records from the transducer is set forth in Figure 1. A relatively high-frequency harmonic is apparently superimposed upon the measured pressure perturbations. These high-frequency oscillations are believed to represent nothing other than noise in the pickup circuit and correspond roughly to the natural frequency of the condenser-type transducer.

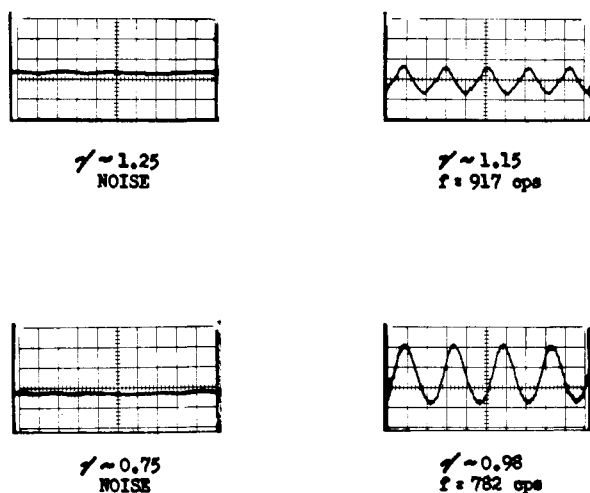


Figure 1. Typical oscillograph records at an approach velocity of approximately 8.6 feet per second

The four typical oscillograph records shown in Figure 1 illustrate behavior under substantially steady combustion at low and high mixture ratios as well as the two typical modes of oscillatory combustion encountered at compositions near stoichiometric. At mixture ratios leaner than stoichiometric the frequency is approximately 780 cycles per second, while above stoichiometric it increases to approximately 920 cycles per second and remains very near this value over a range of mixture ratios. As was indicated earlier, the frequency of the superimposed oscillation is approximately 13,000 cycles per second and corresponds roughly to the natural frequency of the condenser-type transducer.

After a few days from the time measurements had been recorded at a particular set of conditions, a duplicate set of measurements was made. Therefore, for each set of combustion conditions there was usually a total of eight gas samples from which the oxides of nitrogen were determined, and a total of approximately 12 oscillograph records which indicated the nature of the pressure perturbations. This large number of essentially duplicate measurements was necessary to obtain a reasonable measure of the standard deviation in the experimental measurements, particularly in connection with the magnitude of the pressure perturbations. The pressure perturbations appear especially sensitive to minor changes in combustion conditions. The results presented are believed to be typical of the behavior encountered under these conditions of combustion within the limits established by the indicated standard deviation of the experimental data. The number of measurements taken at each set of conditions was sufficient to make conventional statistics pertinent.

MATERIALS

The air employed for this investigation was drawn from outside the laboratory and filtered through charcoal. The natural gas was supplied by the Southern California Gas Company at a pressure of 18 pounds per square inch absolute. It was substantially in equilibrium with water under these conditions, and a typical analysis with a measured value of specific weight is presented in Table I. As a result of minor changes in specific weight, as measured with gas-density balance at the time each set of measurements was made, the relative quantities of methane and ethane were adjusted to yield satisfactory agreement with the measured specific weight. The maximum change in composition from that shown in the typical analysis of

Table I. Natural Gas Analysis

Component		Quantity Mole Fraction
Methane	CH ₄	0.8945
Ethane	C ₂ H ₆	0.0736
Propane	C ₃ H ₈	0.0182
1-Butene	C ₄ H ₈	0.0012
Iso-Butane	C ₄ H ₁₀	0.0008
n-Butane	C ₄ H ₁₀	0.0022
1-Pentene	C ₅ H ₁₀	0.0006
Iso-Pentane	C ₅ H ₁₂	0.0014
n-Pentane	C ₅ H ₁₂	...
Hydrogen	H ₂	...
Nitrogen	N ₂	...
Carbon Monoxide	CO	...
Carbon Dioxide	CO ₂	0.0071
Argon	A	0.0003
Molecular Weight		18.0786

Table I was 0.005 mole fraction ethane. This procedure is believed to have permitted a satisfactory first-order correction for the minor changes of relative amounts of methane and ethane present in the gas.

EXPERIMENTAL RESULTS

A typical set of experimental conditions is portrayed as a function of time in Figure 2. The exit temperature of cooling water and the reactant temperature are included. Figure 3 presents the frequency and double amplitude of the perturbations, the residual mole fraction of nitrogen oxides as found by conventional sampling techniques at the centerline of the reactor 100 inches above the flameholder, and the weight rate of flow of the reactants. Corresponding standard deviations calculated by

$$S = \left\{ \frac{\sum (\bar{x} - x_i)^2}{N} \right\}^{1/2} \quad (1)$$

are included for each variable. The associated mean values are shown by a horizontal broken line. The times indicated on the abscissa were measured from the initiation of combustion. Variation in behavior with time as presented in Figures 2 and 3 is rather typical of that found for other combustion conditions.

A summary of the experimental conditions investigated is set forth in Table II. The standard deviation experienced

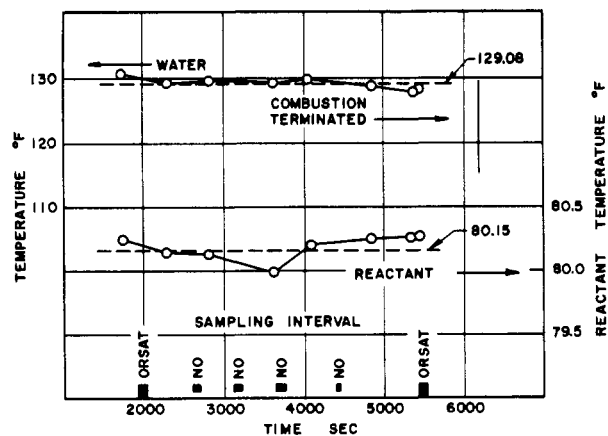


Figure 2. Variation in temperature of reactants and cooling water

Table II. Experimental Conditions

Natural Gas										Air				
No. of points	Weight Rate of Flow, lb./ (sec.) (sq. ft.)		Temperature ° F.		Mixture ratio fraction stoichiometric	Pressure average p.s.i.a.	Test No.	Duration Sec.	No. of points	Weight Rate of Flow lb./ (sec.) (sq. ft.)		Temperature ° F.		Water weight fraction
	Average	Standard deviation	Average	Standard deviation						Average	Standard deviation	Average	Standard deviation	
3	0.02955	0.00004	88.16	0.51	0.76	14.282	359	6754	3	0.6375	0.0009	74.86	0.46	0.0111
3	0.03180	0.00003	91.28	0.17	0.84	14.249	360	6190	3	0.6236	0.0011	73.55	0.57	0.0112
3	0.02902	0.00001	87.56	0.47	0.75	14.263	361	7590	3	0.6373	0.0009	75.77	0.40	0.0101
3	0.03166	0.00003	90.98	0.37	0.83	14.257	362	7620	3	0.6269	0.0009	72.98	0.50	0.0106
1	0.03013	...	89.78	...	0.78	14.281	367	1150	1	0.6342	...	76.21
1	0.03090	...	90.14	...	0.81	14.268	...	1770	1	0.6313	...	75.60
1	0.03213	...	91.04	...	0.84	14.264	...	1515	1	0.6336	...	74.84
1	0.03643	...	91.04	...	1.00	14.267	...	1855	1	0.5993	...	75.12
1	0.04232	...	91.40	...	1.15	14.262	...	2270	1	0.6069	...	74.01	...	0.0101
1	0.04745	...	91.04	...	1.27	14.266	...	1174	1	0.6191	...	74.22
1	0.04477	...	90.68	...	1.21	14.261	...	1422	1	0.6127	...	74.35
1	0.03275	...	88.16	...	0.87	14.282	368	871	1	0.6910	...	75.53
1	0.03434	...	88.70	...	0.92	14.282	...	1251	1	0.6182	...	75.31
1	0.03804	...	89.24	...	1.05	14.283	...	1092	1	0.6136	...	74.58
1	0.04027	...	89.88	...	1.11	14.282	...	1967	1	0.5994	...	75.67
1	0.04550	...	90.32	...	1.23	14.279	...	1259	1	0.5987	...	75.79
1	0.04819	...	91.04	...	1.29	14.285	...	2180	1	0.6110	...	75.32
1	0.05595	...	91.04	...	1.48	14.290	...	1707	1	0.6172	...	75.22
1	0.02790	...	91.40	...	0.72	14.285	...	2679	1	0.6261	...	74.44	...	0.0116
3	0.02945	0.00002	88.82	0.17	0.76	14.267	376	4800	3	0.6429	0.0005	75.41	0.38	0.0074
3	0.02963	0.00002	90.14	0.15	0.76	14.187	377	4350	3	0.6408	0.0009	75.43	0.17	0.0059
3	0.03227	0.00001	88.22	0.08	0.86	14.210	378	4060	3	0.6167	0.0010	74.95	0.21	0.0082
3	0.03280	0.00010	88.82	0.22	0.88	14.232	379	3546	3	0.6167	0.0000	75.06	0.28	0.0088
3	0.03625	0.00002	88.34	0.00	0.98	14.192	380	3275	3	0.6121	0.0006	76.70	0.07	0.0078
3	0.03649	0.00003	84.92	0.15	1.00	14.214	382	3976	3	0.6020	0.0001	77.87	0.04	0.0052
3	0.04246	0.00003	84.56	0.00	1.15	14.266	383	4160	3	0.6102	0.0016	77.96	0.25	0.0048
3	0.04220	0.00001	86.24	0.08	1.15	14.151	384	3582	3	0.6075	0.0012	77.37	0.17	0.0054
3	0.04661	0.00001	84.92	0.39	1.24	14.164	385	4410	3	0.6202	0.0002	77.74	0.03	0.0076
3	0.04690	0.00002	84.56	0.00	1.25	14.156	386	5172	3	0.6181	0.0003	77.86	0.24	0.0068
3	0.03412	0.00003	87.62	0.15	0.93	14.323	391	6800	3	0.6036	0.0007	76.19	0.40	0.0068
3	0.03890	0.00002	87.56	0.17	1.09	14.348	392	5597	3	0.5915	0.0004	77.08	0.41	0.0048
3	0.03387	0.00008	85.40	0.37	0.93	14.327	393	6226	3	0.5987	0.0005	77.00	0.12	0.0043
3	0.03872	0.00002	85.46	0.15	1.08	14.295	394	6578	3	0.6009	0.0004	74.88	0.05	0.0097
3	0.03896	0.00004	90.62	0.47	1.07	14.270	399	6690	3	0.6057	0.0011	76.25	0.44	0.0098
3	0.03911	0.00006	87.98	0.25	1.07	14.295	3

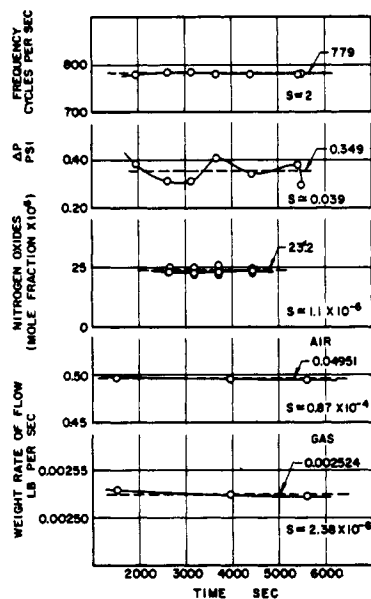


Figure 3. Deviations from steady conditions

from the mean, as well as the total elapsed time when measurements were obtained, are portrayed for each variable. Table III presents a similar summary of the nature of perturbations encountered, and gives the double amplitude of the pressure perturbations, the frequency, and a qualitative description of the flame. The information in the two tables may be related through the test number.

From a review of Table III it is apparent that the perturbation frequency exhibits a much smaller relative standard deviation than does the double amplitude of the pressure fluctuation. To illustrate this situation, Figure 4 shows the frequency of pressure perturbations, the double amplitude, and the mole fraction nitrogen oxides as a function of fraction of the population upon a probability scale. These data clearly indicate that the frequency of the perturbations and the mole fraction of residual oxides of nitrogen are relatively stable at a particular set of operating conditions. However, the magnitude of the double amplitude of the pressure fluctuations varies markedly. The situation shown in Figure 4 is typical of that encountered in nearly all the experimental work. In other words, as shown in Table III, the relative standard deviation for the

Table III. Summary of the Nature of Perturbations^a

Test No.	Duration Sec.	No. of points	Transient Pressure		No. of points	Frequency		No. of points	Oxides of Nitrogen		Flame Description
			ΔP P.S.I.			cycles/sec.			Mole Fraction		
			Average	Standard deviation		Average	Standard deviation		Average	Standard Deviation	
Grid VII-C with 4 Vane Baffle											
359	3254	6	0.109	0.048	5	48	28	12	13.2×10^{-6}	1.5×10^{-6}	Quiet and steady
360	1868	7	0.342	0.039	7	779	2	12	23.2	1.1	Oscillatory
361	2020	7	0.095	0.021	12	8.5	0.6	Quiet and steady
362	2012	7	0.221	0.077	5	711	8	12	25.2	0.7	Oscillatory
367	325	Quiet and steady
	360	3	0.232	0.049	3	843	20	Oscillatory
	205	3	0.461	0.021	3	778	3	Oscillatory
	192	3	0.641	0.017	3	926	1	Oscillatory
	1744	5	0.612	0.039	5	939	4	Oscillatory
	198	Irregular
	276	3	0.381	0.042	3	950	4	Oscillatory
368	152	3	0.593	0.026	3	775	1	Oscillatory
	210	3	0.566	0.018	3	787	0	Oscillatory
	1256	3	0.654	0.009	3	921	7	Oscillatory
	160	3	0.890	0.056	3	920	2	Oscillatory
	393	4	0.504	0.094	4	879	4	Oscillatory
	154	Irregular
	100	Flame Out
	163	Irregular
376	2776	8	17.4×10^{-6}	0.8×10^{-6}	Quiet and steady
377	2618	8	13.4	1.9	Quiet and steady
378	2451	12	0.656	0.067	12	765	2	8	26.8	0.3	Oscillatory
379	2263	12	0.635	0.045	12	766	4	8	27.8	1.4	Oscillatory
380	2127	12	0.636	0.065	12	785	3	8	43.0	2.0	Oscillatory
382	2306	12	0.698	0.060	12	908	4	8	22.3	3.7	Oscillatory
383	2324	12	0.427	0.087	12	923	5	7	2.7	0.8	Oscillatory
384	2457	12	0.421	0.088	11	926	11	8	1.8	0.6	Oscillatory
385	2220	8	3.7	1.3	Quiet and irregular
386	2176	8	7.9	1.7	Quiet and irregular
391	4328	12	0.699	0.092	12	776	8	12	39.9	1.7	Oscillatory
392	3885	12	0.656	0.168	12	922	3	12	12.7	8.0	Oscillatory
393	4976	12	0.606	0.074	12	778	10	12	43.6	1.5	Oscillatory
394	3912	12	0.232	0.035	12	918	6	12	24.2	8.4	Oscillatory
398	4600	12	0.623	0.196	12	926	4	11	24.6	7.6	Oscillatory
399	4987	12	0.493	0.070	12	923	2	10	14.5	9.2	Oscillatory

^a Daily run averaged and a standard deviation obtained.

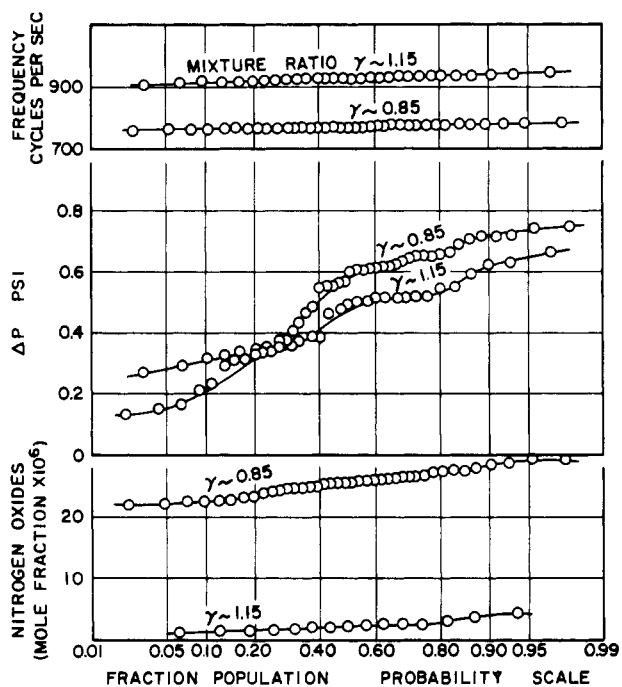


Figure 4. Variation in frequency, double amplitude, and oxides of nitrogen for mixture ratios of 0.85 and 1.15

double amplitude of the pressure deviation is many times that of the frequency and quantity of the oxides of nitrogen. Cause for the much wider fluctuations in the pressure amplitude is not clearly understood at present. Earlier studies (1) indicate that minor changes in the reactant velocity do not appreciably influence the behavior of the pressure perturbation. However, the magnitude of the perturbations is much more susceptible to the kinetics of the reaction than is the frequency of perturbations. Microscopic consideration of changes in chemical composition associated with the perturbations is probably necessary before factors leading to the marked variation in double amplitude of pressure perturbations at a given macroscopic steady state may be understood.

Figure 5 presents average values of nitrogen oxides as a function of mixture ratio for a reactant velocity of approximately eight feet per second. Values of the reactant velocity which vary between 8.2 and 9.0 feet per second have been nominally treated as 8.6 feet per second. Standard deviation of the data and the number of analyses

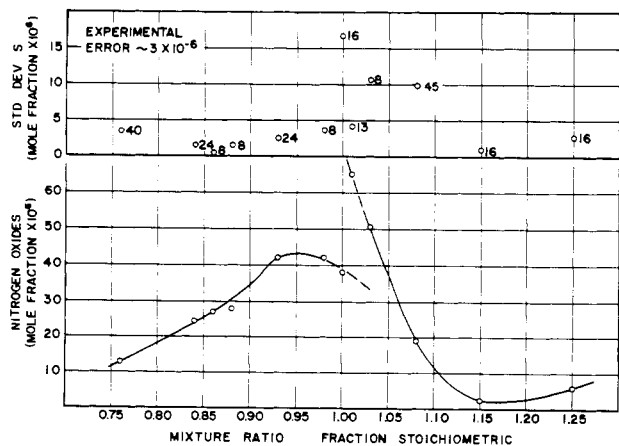


Figure 5. Effect of mixture ratio on average mole fraction oxides of nitrogen

involved are shown in the upper part of the figure. In addition, the estimated experimental error in the analytical procedure of 3×10^{-6} mole fraction has been included. The standard error of estimate of the average values for each test condition from the smooth curve shown was 0.8×10^{-6} mole fraction.

Near stoichiometric, particularly on the rich side, it should be noted that the standard deviation is many times as great as in other parts of the diagram. Measurements were carried out at three widely-separate times at a mixture ratio of approximately 1.08. The results were similar and deletion of any one set of measurements did not significantly change the average behavior shown. The marked change in the residual quantities of nitrogen oxides at or near stoichiometric is surprising, but such a discontinuous change was reflected in other measured quantities as well.

The mole fraction of carbon monoxide, oxygen, and carbon dioxide, as determined from Orsat analyses, is constituted in Figure 6. Behavior was in accordance with expectations. Presented for comparison are the predicted quantities of each component at stoichiometric mixture ratio for physicochemical equilibrium at the adiabatic flame temperature. The quantities of carbon monoxide found were smaller than those corresponding to physicochemical equilibrium, while the quantities of carbon dioxide were larger.

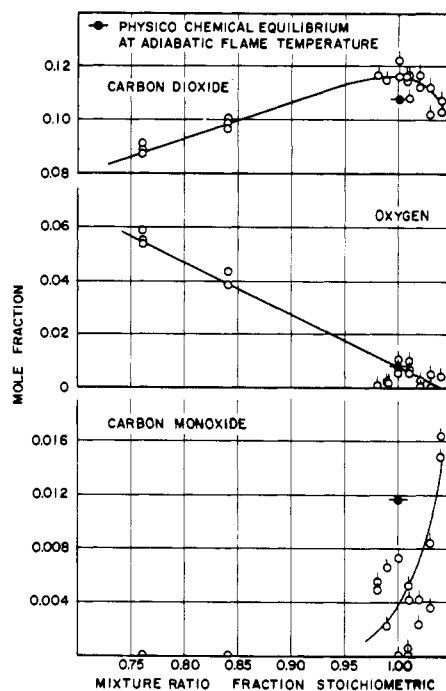


Figure 6. Mole fraction of principal products of reaction as a function of mixture ratio

Variation in the frequency of perturbations with mixture ratio is depicted in Figure 7. The upper part of the figure presents the standard deviation of the data from the average and the number of measurements involved at each mixture ratio. The standard deviation, except in the immediate vicinity of stoichiometric and for extremely rich mixtures, is only two or three times the experimental error involved in measuring the frequency. There is a discontinuous shift in the frequency near stoichiometric, and under one set of conditions it was possible to obtain the higher frequency at mixture ratios less than stoichiometric, while the lower frequency was realized for most of the data at the same mixture ratio.

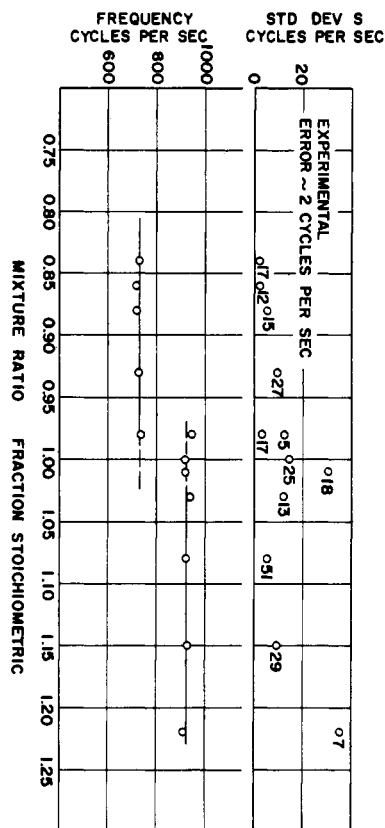


Figure 7. Characteristic average frequencies encountered in perturbations

Information obtained at several mixture ratios was measured over a period of several months and indicates the stability of the characteristic frequencies. The nature of the pressure perturbations for the two characteristic frequencies is shown on the right-hand side of Figure 1, as was discussed earlier.

Figure 8 depicts the pressure fluctuations measured with the flush-mounted, condenser-type transducer. The standard deviation of the experimental data from the average at each mixture ratio is presented in the upper part of the figure, along with the number of experimental measurements carried out at each mixture ratio. The discontinuity near stoichiometric is not so pronounced and would

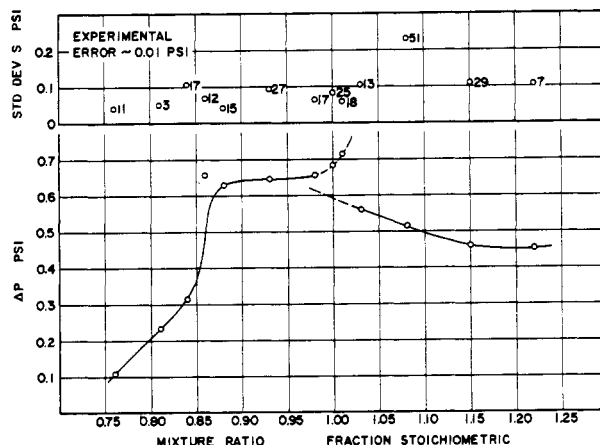


Figure 8. Effect of mixture ratio on average double amplitude of pressure perturbations

Table IV. Average Behavior of Combustion Process^a

No. of Points	Mixture Ratio Fraction Stoichiometric		Transient Pressure						Oxides of Nitrogen Mole Fraction		
	Average	Standard Deviation	ΔP P.S.I.			Frequency Cycles/Sec.			Average	Standard deviation	Relative percent
			Average	Standard Deviation	Relative percent	Average	Standard Deviation	Relative percent			
13	0.76	0.0050	0.106	0.038	35.7
40	0.76	0.0046	12.7×10^{-6}	3.4×10^{-6}	26.7
3	0.81	...	0.232	0.049	21.1	843	20	2.37
17	0.84	0.0049	0.313	0.104	33.2	779	2	0.26
24	0.84	0.0050	24.2	1.4	5.6
12	0.86	...	0.656	0.067	10.2	765	2	0.26
8	0.86	26.8	0.3	1.1
15	0.88	0.0040	0.627	0.041	6.54	768	5	0.65
8	0.88	27.8	1.4	5.0
27	0.93	0.0031	0.643	0.092	14.3	777	9	1.16
24	0.93	41.8	2.4	5.8
17	0.98	...	0.654	0.063	9.6	785	3	0.38
5	943	12	1.27
8	0.98	41.9	3.6	8.5
25	1.00	0.0040	0.682	0.081	11.9	916	14	1.53
16	1.00	0.0043	37.8	16.7	44.3
18	1.01	0.0042	0.713	0.058	8.1	914	30	3.28
13	1.01	0.0046	65.1	4.1	6.3
13	1.03	0.0077	0.557	0.183	32.8	938	12	1.28
8	1.03	0.0050	50.5	10.6	20.9
51	1.08	0.0111	0.524	0.228	43.5	922	5	0.54
45	1.08	0.0083	18.8	9.9	52.7
29	1.15	...	0.457	0.108	23.6	927	9	0.97
16	1.15	2.2	0.9	38.8
7	1.22	0.0100	0.451	0.105	23.3	910	35	3.85
16	1.25	0.0050	5.8	2.6	45.2

^a All runs of similar conditions averaged and a standard deviation, S, obtained

probably not be considered significant if the discontinuity in frequency had not been so well established. It should be emphasized that the relative standard deviation in the case of a double amplitude of pressure fluctuation is much greater than the comparable information for the frequency and the mole fraction of the oxides of nitrogen.

The total experimental data yielded a standard error of estimate from the smooth curve at mixture ratios less than stoichiometric of 0.088 pound per square inch and at mixture ratios greater than stoichiometric of 0.193. For mixture ratios between unity and 1.10 there is a rapid increase in the standard error of estimate, which approaches a value of approximately 50 per cent of the average value at a mixture ratio of 1.08.

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Thermal Conductivity of Fluids. Nitrous Oxide

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A knowledge of the molecular thermal conductivity of nitrous oxide is important in predicting thermal transfer to this fluid under many of the conditions encountered in industrial practice. Available experimental information is limited. In this study, data concerning the thermal conductivity of nitrous oxide were taken at temperatures from 40° to 340° F. and at pressures up to 5000 pounds per square inch. Data near the critical state were not obtained due to the persistence of natural convection, even when the temperature gradients were small. The data show the normal trends in thermal conductivity with respect to variation in both pressure and temperature. No difficulty from thermal instability of the nitrous oxide was encountered.

IT IS NOT YET feasible to predict the molecular thermal conductivity of fluids at elevated pressures with an accuracy sufficient for engineering needs. Furthermore, experimental data are limited even for fluids of industrial importance. Keyes (8) recently made an excellent survey of the experimental data available for a number of gases. Sellschopp (14) and Vargaftik (15) studied the thermal conductivity of gases at high pressures, and Mason (10) reported the thermal conductivity of a number of liquids in the temperature range between 32° and 312° F.

Johnston and Grilly (7) and Eucken (2) measured the thermal conductivity of nitric oxide at atmospheric pressure, and Richter (13) investigated the effect of pressure and temperature upon the thermal conductivity of nitric oxide. Richter (12) also studied the thermal conductivity of nitrogen dioxide in the liquid phase at temperatures up to 160° F.

Experimental measurements of the thermal conductivity of nitrous oxide were reported by Keyes (9) for pressures up to 775 pounds per square inch at 122° F., and by