An Experimental Study of the Formation and Decomposition of Nitric Oxide

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THE PRIMARY reaction involved in the formation and decomposition of nitric oxide is described by Equation 1:

$$2\,NO \rightleftarrows N_2 + O_2 \qquad (1)$$

Nerst (*8*) and Jellinek (*4*) evaluated the equilibrium of the reaction described by Equation 1 and expressed results in terms of an equation constant defined as follows:

$$\frac{(NO)_e^2}{(N_2)_e(O_2)_e} = K = \frac{k_2}{k_1} \qquad (2)$$

Values of this conatant were tabulated by Rossini (*11*). Penner (*10*) studied many aspects of the formation and decomposition of the oxides of nitrogen, and Vetter (*12*) and Wise (*14*) considered the influence of oxygen as a catalyst in accelerating the decomposition of nitric oxide.

Figure 1 presents semiquantitatively the effects of temperature upon the equilibrium mole fraction of nitric oxide for a pressure of 1000 p.s.i. In carrying out these calculations, it was assumed that there were equal mole fractions of nitrogen and oxygen initially. Only the reactions pertaining to the formation of nitric oxide from nitrogen and oxygen and the formation of monatomic nitrogen and oxygen from diatomic nitrogen and oxygen were considered. Account was taken of the fact that the formation of monatomic oxygen tends to increase the mole fraction of nitric oxide at the higher pressures. The data compiled by Lewis and von Elbe (*5*) were employed.

Figure 1 also shows the mole fraction of nitric oxide which remains after cooling the system at different rates of temperature change. This latter information was obtained following the general methods suggested by Altman and Penner (*1*). Kinetics data of the form suggested by Gilbert and Daniels (*3*) were employed to establish the curves. The mole fraction of nitric oxide at equilibrium increases in a regular fashion with an increase in temperature, and it is possible to take advantage of the increased mole fraction of nitric oxide, if a high rate of cooling is utilized. A rate of cooling of at least 10^8 ° R. per second is required to obtain more than 0.04 mole fraction nitric oxide.

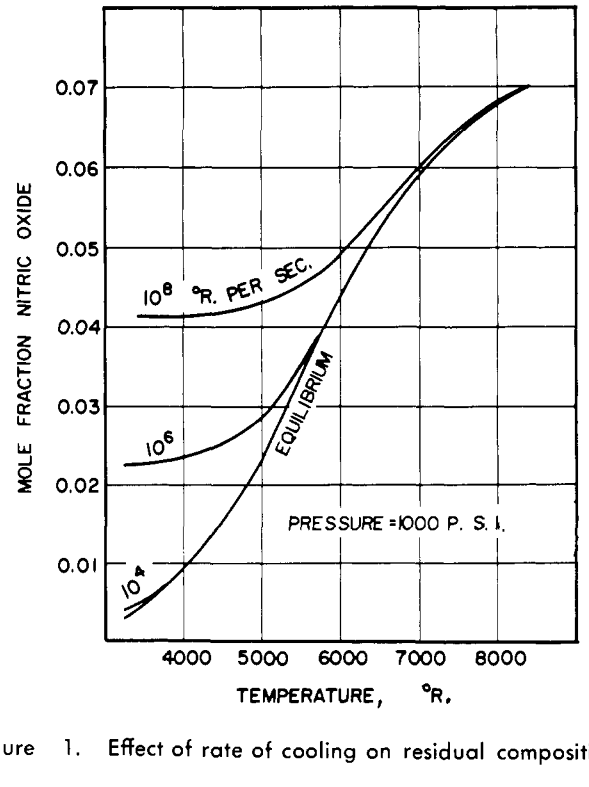

Figure 1. Effect of rate of cooling on residual composition

EQUIPMENT

For the present investigation a ballistic piston apparatus (*7*) was used. Figure 2 shows, schematically, the heavy-walled cylinder, *A*, within which the piston, *B*, moved. The sample was confined in the space, *C*, beneath the piston. Compressed gas contained in the space, *D*, drove the piston following its release by a shear pin, *E*. Electrical contacts, *F*, were used to determine the position of the piston as a function of time. The composition of the initial gas sample, the thermal transfer from the sample, and the composition of the gas sample after compression also were determined. Pressure ratios as high as 100,000 to 1 were obtained, and by appropriate choice of diluent gases it was possible to reach energies equivalent to apparent temperatures of 100,000 ° R.

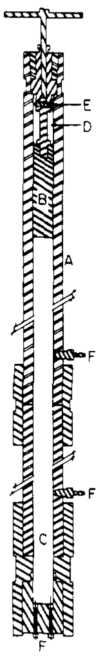

Figure 2. Schematic diagram of apparatus

Figure 3 illustrates the general nature of the temperature-time relationship during typical compression cycles involving the heavy and light pistons used. The data show that the temperature course of the compression and expansion above 3000° R. was limited to approximately 4 milliseconds for the light piston and to approximately 7 milliseconds for the heavy piston. The temperature data of Figure 3 were obtained by calculations assuming isentropic compression and expansion and no chemical reaction,

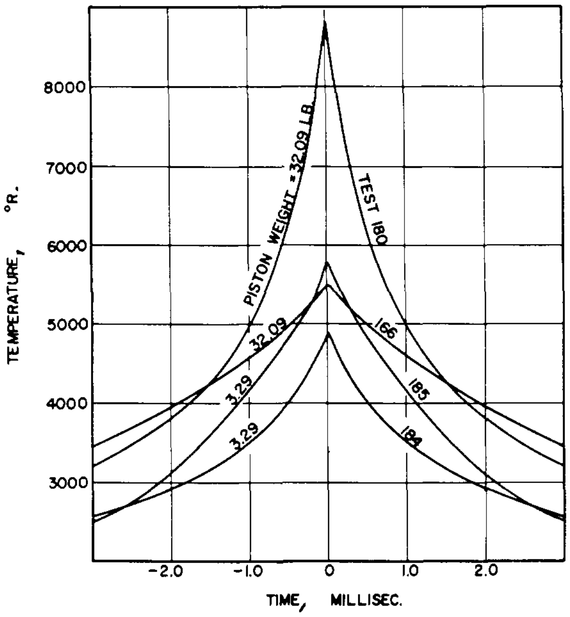

Figure 3. Temperature-time relations for two pistons for a composition of 0.4 mole fraction nitrogen, 0.2 mole fraction oxygen, and 0.4 mole fraction helium.

whereas the time data were based on actual measurements made on the downstroke of the piston during each test. Throughout this article, the term temperature used in connection with the state of the sample refers to apparent temperature.

METHOD OF ANALYSIS

Measurements of the temperature and pressure of each component of the initial gas sample were made during introduction to the sample chamber. For most of the tests, the composition of the initial sample was established from these data. In the 13 earliest tests, mass spectrographic analyses were made on samples of the initial gas which were withdrawn following introduction to the sample chamber.

After compression, samples of the product were withdrawn and stored in sealed glass bulbs. The product compositions for the first 19 tests were determined by mass spectrographic analysis. This technique was unsatisfactory for the determination of the oxides of nitrogen, however, and it was replaced by a chemical procedure involving titrimetric methods (*2*). This procedure involved introduction of the gas sample to an evacuated flask containing a neutral hydrogen peroxide solution. The oxides of nitrogen were converted to nitric acid which was titrated with standard alkali. Experience with these analytical techniques indicated that the mole fraction of oxides of nitrogen could be determined within 0.001. Results which showed a larger deviation were included only in a few instances to show a trend in a region where no other data were at hand.

EXPERIMENTAL RESULTS

The experimental conditions for each of 65 tests upon the nitrogen-oxygen system are set forth in Table I. The maximum apparent temperatures given in Table I were calculated (*6, 7*) from measurements of the closest approach of the piston to the bottom of the cylinder, assuming isentropic compression and no chemical reaction. The maximum pressure ratio given in the table is defined as the ratio of the maximum pressure attained by the sample to the initial pressure of the sample. The conditions set forth for minimum volume are subject to uncertainty, but they present the trends in the results.

The relative thermal transport from the sample (Table I) is expressed as the ratio between the thermal transfer from the sample and the maximum apparent energy transferred to the sample by compression. These data indicate a trend toward an increase in the fractional energy loss as the apparent temperature increases. The entire thermal transfer was established by measuring the radiant and convective transfer to a small area at the bottom of the compression chamber and applying this value per unit area to the face of the piston and bottom of the compression chamber. The varying area associated with the cylinder walls was neglected. The thermal transfer to the piston face and the bottom of the compression chamber may amount, in the case of the higher temperatures, to as much as 13% of the total energy added to the sample.

If the shear along the walls is neglected, the temperature distribution within the sample is nonuniform for a distance amounting to approximately 5% of the radius of the cylinder (*13*). Beyond this area near the walls, within which conduction to the walls exerts an influence, the sample is of a relatively uniform energy content with respect to the spatial coordinates of the sample.

Table II presents the initial and final compositions for the 65 tests. Helium was employed as an initial component in order that the fugacity-temperature relationship of the other components could be varied independently. From a kinetics standpoint, the helium undoubtedly influenced the rate of reaction because it acts as a major diluent. The final compositions are expressed in terms of mole fractions of nitric oxide, although at room temperature a substantial part of the nitric oxide reacted with the remaining oxygen to form nitrogen tetroxide. Table II also includes a residual nitric oxide ratio which is the ratio of the square of the mole fraction of nitric oxide to the product of the mole fraction of nitrogen and oxygen remaining in the product. The values were based on the assumption that all the residual oxides of nitrogen were nitric oxide. This ratio provides a convenient means of comparing the behavior of samples of differing compositions which underwent the same environmental compression cycle.

The influence of the maximum apparent temperature upon the residual nitric oxide ratio is shown in Figures 4 to 6 for compositions containing 0.4 mole fraction nitrogen, 0.2 mole fraction oxygen, and 0.4 mole fraction helium. The data of Figure 4, limited to an initial sample pressure of approximately 1.16 p.s.i., include information for both the light and heavy piston. A markedly higher nitric oxide ratio for the same maximum apparent temperature was found for the tests in which the light piston was used. In Figure 5, the initial sample pressure of approximately 2.31 p.s.i. is nearly twice the pressure in Figure 4. At this higher pressure, the smaller difference in rates of cooling between the tests made with the light piston and those made with the heavy piston produced a smaller difference in the residual amount of nitric oxide than was found at the lower pressure associated with the data depicted in Figure 4. Figure 6 presents data for an initial sample pressure of approximately 4.62 p.s.i. which shows much less, if any, difference between the behavior with the light and the heavy piston.

Figure 7 shows that variation in the nitrogen-oxygen ratio has a relatively small influence upon the relationship of the residual nitric oxide ratio to the maximum apparent temperature. Measurements upon the two compositions illustrated were made with a piston which weighed 3.29 pounds. The straight lines were fitted to the points by a least squares method (*9*). The residual nitric oxide ratio is roughly 0.0005 larger for the mixture containing the smaller quantity of oxygen. In each case, the original sample contained 0.8 mole fraction helium. These limited data illustrate the measurable influence of oxygen upon the decomposition of nitric oxide, as reported by Vetter (*12*) and Wise (*14*).

Approach to chemical equilibrium in the ballistic piston

Table I. Experimental Conditions for Nitrogen-Oxygen System Tests

		Initial Conditions[a]			Conditions at Minimum Volume[b]						
Test No.	Piston Weight, Lb.	Driving air pressure, p.s.i.	Initial sample pressure, p.s.i.	Sample volume, cu. ft.	Piston approach, in.	Volumetric compression ratio	Maximum apparent temp., ° R.	Maximum apparent pressure, p.s.i.	Maximum pressure ratio	Relative Thermal Transport $\underline{Q}/\Delta\underline{E}$	Rate of Temp. Change ° F./sec.
133	2.44	684.9	3.100	0.4282	0.1583	55.30	5100	22300	7200		...[c]
136	2.44	570.5	2.098	0.4282	0.1414	61.93	7800	24800	11800	...	...
391	3.28	343.6	2.872	0.4282	0.9830	8.894	7000	4000	1400	0.05115	0.868
392	3.28	500.0	2.881	0.4282	0.4709	18.57	10300	12700	4400	0.08948	2.093
394	3.28	292.5	2.869	0.4282	1.2020	7.274	6300	2900	1000	0.04981	0.782
395	3.28	238.1	2.883	0.4282	1.9601	4.483	4900	1400	500	0.03276	...
397	3.28	406.1	2.880	0.4283	0.6879	12.70	8500	7200	2500	...	1.453
399	3.28	344.7	2.888	0.4283	0.9691	5.716	7100	4300	1500	0.07909	0.991
401	3.28	400.9	2.884	0.4283	0.7021	12.55	8400	6900	2400	0.07241	1.420
402	3.28	473.4	2.879	0.4283	0.5661	15.61	9400	9500	3300	0.05063	1.808
403	3.28	311.9	2.893	0.4283	1.0969	7.966	6600	3400	1200	...	0.803
405	3.28	270.0	2.880	0.4283	1.4177	6.162	5800	2300	800	0.07236	0.585
406	3.28	240.2	2.887	0.4283	1.8452	4.739	5100	1400	500	0.05134	0.351
407	3.28	301.7	2.888	0.4283	1.3994	6.243	5800	2300	800	0.08449	0.651
408	3.28	344.7	2.873	0.4283	1.1374	7.676	6500	3200	1100	0.07322	0.897
409	3.28	400.8	2.887	0.4283	0.6949	12.58	8400	6900	2400	0.10140	1.321
154	3.29	522.5	2.309	0.4282	0.2223	39.36	6900	14800	6400	...	1.418
162	3.29	607.1	2.307	0.4282	0.2224	39.35	6900	14700	6400	...	2.184
163	3.29	715.4	4.612	0.4282	0.6635	13.17	4600	6500	1400	...	0.937
178	3.29	1083.0	4.633	0.4282	0.2025	43.18	7400	38900	8400	0.07685	2.551
179	3.29	275.4	1.061	0.4282	0.2048	42.70	7000	7200	6800	0.07232	1.254
184	3.29	240.6	1.191	0.4282	0.5485	15.93	4900	2100	1800	...	...
185	3.29	216.3	1.160	0.4282	0.3525	24.81	5800	3800	3300	...	0.768
310	3.29	317.1	2.878	0.4282	1.3900[d]	6.281	5900[d]	2400[d]	850[d]	...	...
313	3.29	460.1	2.880	0.4282	1.2080[d]	7.228	6300[d]	3000[d]	1000[d]	...	...
315	3.29	600.1	2.887	0.4282	0.5468	15.99	9600	10100	3500	0.13290	1.217
317	3.29	317.0	2.869	0.4282	1.5730[d]	5.550	5500[d]	2000[d]	690[d]	...	...
319	3.29	460.1	2.878	0.4282	1.1900	7.338	6400	3200	1100	...	...
321	3.29	600.1	2.885	0.4282	0.5354	16.33	9700	10400	3600	0.07063	0.658
146	3.38	555.1	2.115	0.4282	0.1333	6.547	8000	13100	27700	...	...
149	3.38	207.9	1.160	0.4282	...	...	...	...	...	...	...
150	3.38	437.8	2.310	0.4282	0.3423	25.54	5900	8300	3600	...	1.444
152	3.38	897.3	4.616	0.4282	0.2987	29.27	6300	20800	4500	...	1.925
158	3.38	240.5	1.148	0.4282	0.4505	19.39	...	...	...	...	...
36	30.94	999.1	2.963	0.4070	0.1104	75.14	5100	25000	8400	...	...
38	30.96	1004.0	2.297	0.4071	...	...	...	...	...	...	...
39	30.96	580.8	2.261	0.4071	0.2577	32.20	4500	7400	3300	...	...
40	30.96	688.0	1.892	0.4071	>0.1592	...	< 8600	< 19200	< 10100	...	...
41	30.96	688.0	1.877	0.4071	0.1803	52.09	8300	16200	8600	...	...
42	30.96	1004.0	2.200	0.4071	0.1735	...	13900	33000	15000	...	...
43	30.96	718.4	2.153	0.4071	0.2913	28.47	8500	11900	5500	...	...
44	30.96	917.6	3.206	0.4071	0.1942	42.73	4800	14700	4600	...	...
45	30.96	524.6	2.019	0.4071	0.3441	24.12	5800	6300	3100	...	...
48	30.96	481.7	2.021	0.4071	0.3495	23.76	4500	4900	2400	...	...
49	30.96	638.9	1.942	0.4071	0.2875	28.87	9100	11300	5800	...	...
50	30.96	718.6	2.140	0.4071	0.2121	39.14	9800	18200	8500	...	...
51	30.96	609.3	2.174	0.4071	0.2768	29.98	8700	12700	5800	...	...
114	30.98	715.5	2.762	0.4071	0.2228	37.34	5000	12700	4600	...	...
115	30.98	716.6	2.774	0.4071	0.2165	38.41	5000	12700	4600	...	...
116	30.98	716.5	2.770	0.4071	0.2232	37.25	5000	12700	4600	...	...
117	30.98	716.6	2.767	0.4071	0.2067	40.23	5100	13800	5000	...	...
337	32.04	460.2	2.874	0.4070	0.7358	11.28	7900	5700	2000	...	...
342	32.04	317.0	2.890	0.4070	1.7077	4.861	5100	1500	500	...	...
344	32.04	600.1	2.891	0.4070	0.4868	17.07	9800	11000	3800	...	...
147	32.09	843.0	2.118	0.4068	0.0928	98.84	9200	47000	22200	...	...
151	32.09	264.1	1.155	0.4068	0.3083	26.94	5900	4200	3600	...	0.300
157	32.09	613.3	2.301	0.4068	0.2500	33.23	6500	11700	5100	...	0.566
166	32.09	215.1	1.167	0.4068	0.3779	21.99	5500	3200	2700	...	0.243
171	32.09	1036.0	4.616	0.4068	0.4976	16.69	5000	8800	1900	...	0.391
172	32.09	315.1	1.157	0.4068	0.1511	55.03	7700	11200	9700	...	0.481
175	32.09	740.9	2.343	0.4068	0.1634	50.88	7700	22700	9700	...	...
176	32.09	488.7	2.315	0.4068	0.4161	19.96	5400	6000	2600	...	...
180	32.09	366.2	1.158	0.4068	0.1009	82.55	8900	19700	17000	0.08520	0.683
181	32.09	871.7	2.296	0.4068	0.1049	77.54	9300	46200	20100	0.07858	1.068
182	32.09	1312.0	4.629	0.4068	0.3176	26.14	6000	17600	3800	...	0.532

[a] In Tests 337 through 407 a vent mechanism prevented piston from cscillating.

[b] Closest piston approach measured with a lead gage. Maximum temperatures and pressures calculated from these assuming isentropic compression and no chemical reaction.

[c] Experimental information not available.

[d] Average value.

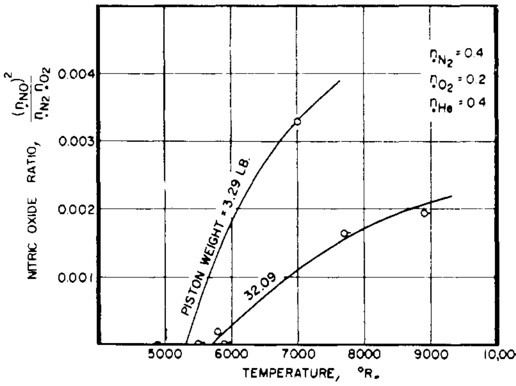

Figure 4. Sample pressure of 1.16 p.s.i.

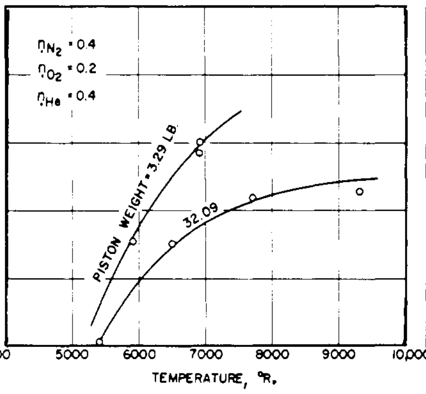

Figure 5. 2.31 p.s.i.

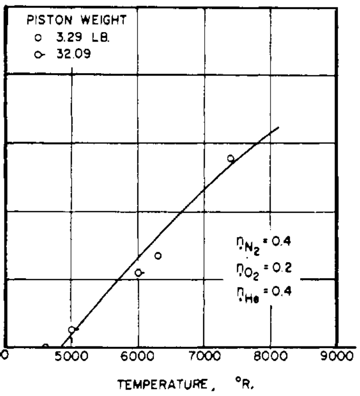

Figure 6. 4.62 p.s.i.

Effect of maximum apparent temperature upon nitric oxide ratio

was established from a series of tests made with the piston weighing 3.29 pounds. Measurements were made upon mixtures which contained equal mole fractions of nitrogen and oxygen with 0.8 mole fraction helium and mixtures which contained 0.2 mole fraction nitric oxide with 0.8 mole fraction helium. The residual nitric oxide ratio resulting from the nitric oxide–helium sample decreased with an increase in the maximum apparent temperature (Figure 8). On the other hand, the residual nitric oxide ratio in the mixture of nitrogen and oxygen increased with an increase in the maximum apparent temperature. Within the uncertainty of measurement, these two mixtures yielded the same residual composition at temperatures of the order of 10,000° R. The residual composition corresponding to a nitric oxide ratio of 1.8×10^{-3} was not the equilibrium composition, but the composition remaining after the sample was subjected to the variable cooling rate associated with these measurements. The maximum cooling rate attained was approximately 2° R. per microsecond.

Figures 9 and 10 show the effect of rate of temperature

Table II. Initial and Final Compositions

Test No.	Initial Composition,[a] Mole Fraction				Final Composition[b]	
	Nitrogen	Oxygen	Nitric oxide	Helium	Nitric oxide,[c] mole fraction	Nitric Oxide ratio[c] $\frac{(n_{NO})^2}{n_{N_2} n_{O_2}}$
133	0.8250	0.1750	...	...	0.0061	0.2615×10^{-3}
136	0.4664	0.1734	...	0.3602	0.0221	6.458
391	0.1002	0.0999	...	0.7999	0.0029	0.8953
392	0.1002	0.0999	...	0.7999	0.0032	1.0433
394	0.1002	0.0999	...	0.7999	0.0019	0.3520
395	0.1002	0.0999	...	0.7999	0.0000	0.0000
397	0.1002	0.0999	...	0.7999	0.0042	1.8585
399	0.1328	0.0673	...	0.8000	0.0034	1.3666
401	0.1328	0.0673	...	0.8000	0.0043	2.129
402	0.1328	0.0673	...	0.8000	0.0038	1.9696
403	0.1328	0.0673	...	0.8000	0.0033	1.3171
405	...	...	0.2007	0.7992	0.0138	21.78
406	...	...	0.2007	0.7992	0.0452	338.15
407	...	...	0.2007	0.7992	0.0146	24.45
408	...	...	0.2007	0.7992	0.0108	13.02
409	...	...	0.2007	0.7992	0.0064	4.379
154	0.3978	0.2008	...	0.4013	0.0147	2.865
162	0.3994	0.2001	...	0.4004	0.0151	3.041
163	0.4008	0.2004	...	0.3988	0.0002	0.0005
178	0.3996	0.2001	...	0.4003	0.0146	2.8085
179	0.3996	0.1999	...	0.4005	0.0156	3.242
184	0.4039	0.2032	...	0.3929	0.0002	0.0005
185	0.4030	0.1966	...	0.4003	0.0041	0.2170
310	...	...	0.1995	0.8005	0.0203	51.12
313	...	...	0.1997	0.8003	0.0090	8.820
315	...	...	0.1999	0.8001	0.0042	1.812
317	0.1010	0.1034	...	0.7956	0.0000	0.0000
319	0.0961	0.0957	...	0.8082	0.0029	0.9657
321	0.1012	0.1012	...	0.7976	0.0042	1.761
146	0.4563	0.1718	...	0.3718	0.0116	1.796
149	0.4000	0.1987	...	0.4013	...	...
150	0.3983	0.1984	...	0.4032	0.0108	1.5485
152	0.4003	0.1998	...	0.3999.	0.0102	1.3715
158	0.4011	0.1993	...	0.3996	...	...
36	0.4626	0.5303	...	0.0044	0.0327	
38	0.1250	0.1248	...	0.7503	0.0102	7.320
39	0.4349	0.4373	...	0.1278	0.0037	0.0723
40	0.2435	0.2438	...	0.5126	0.0198	7.175
41	0.2425	0.2437	...	0.5138	0.0190	6.629
42	0.1251	0.1248	...	0.7501	0.0138	13.67
43	0.1849	0.1839	...	0.6312	0.0129	5.274
44	0.4444	0.4513	...	0.1043	0.0120	0.7413
45	0.4760	...	0.1272	0.3968	0.0457	99.44
48	0.6530	...	0.1644	0.1826	0.0369	29.88
49	0.1794	...	0.1818	0.6388	0.0119	6.406
50	0.1839	0.1845	...	0.6316	0.0050	0.7567
51	0.1846	0.1843	...	0.6312	0.0109	3.744
114	0.4251	0.4246	...	0.1503	...	...
115	0.4258	0.4248	...	0.1494	...	...
116	0.4252	0.4251	...	0.1497	...	...
117	0.4253	0.4253	...	0.1494	...	...
337	0.1009	0.0974	...	0.8016	0.0019	0.3579
342	0.1016	0.1010	...	0.7974	0.0000	0.0000
344	0.1001	0.1019	...	0.7979	0.0044	1.960
147	0.4727	0.1672	...	0.3601	0.0116	1.7785
151	0.3955	0.1980	...	0.4065	0.0008	0.0083
157	0.3995	0.2007	...	0.3997	0.0108	1.521
166	0.3996	0.2001	...	0.4003	0.0002	0.0004
171	0.4005	0.2002	...	0.3992	0.0045	0.2881
172	0.3994	0.2005	...	0.4001	0.0114	1.693
175	0.4008	0.1994	...	0.3998	0.0129	2.194
176	0.3995	0.2005	...	0.4001	0.0020	0.0529
180	0.3996	0.2001	...	0.4004	0.0122	1.951
181	0.3995	0.1994	...	0.4010	0.0132	2.287
182	0.3870	0.2123	...	0.4006	0.0093	1.0945

[a] Initial compositions for Tests 36 through 51 were obtained by mass spectrographic analysis. For the other tests these data were computed from pressure and temperature measurements obtained during addition of the sample gases.

[b] Final compositions for Tests 36 through 136 were obtained by mass spectrographic analysis. For the remaining tests final compositions were obtained by a titrimetric method. The amount of various oxides of nitrogen in the final sample was converted to mole fraction of nitric oxide.

[c] Average of duplicate samples when available. Average deviation of 31 duplicate samples 0.0003 mole fraction nitric oxide and 0.0006 nitric oxide ratio.

change upon the nitric oxide ratio for initial sample pressures of 1.16 and 4.62 p.s.i., respectively. Values of the maximum apparent temperature for each point are included. As expected, there was a marked increase in the nitric oxide ratio with an increase in rate of temperature change. This increase in rate of temperature change, however, was accompanied by a corresponding increase in maximum apparent temperature, which accounts for the disparity between the data for the light and heavy pistons.

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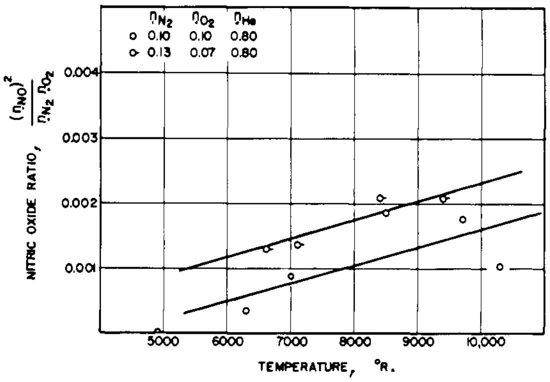

Figure 7. Possible influence of oxygen upon the formation of nitric oxide

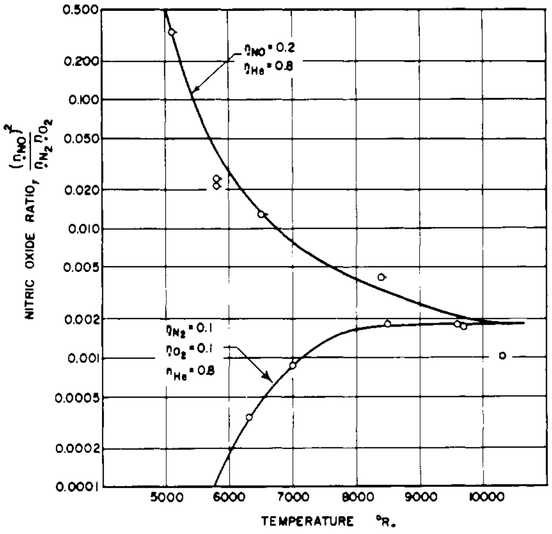

Figure 8. Residual nitric oxide ratio as a function of maximum apparent temperature

NOMENCLATURE

K = equilibrium constant
k_1, k_2 = rate constants
$(N_2),(O_2),(NO)$ = concentrations, lb.-mole/cu. ft.
η_k = mole fraction of component k
Q = total thermal transfer to face of piston and bottom of compression chamber, B.t.u.
T = temperature, ° R.
ΔE = maximum isentropic energy transfer from piston to sample, corresponding to maximum compression, B.t.u.

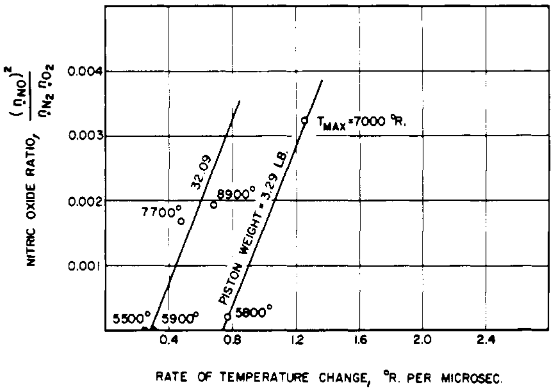

Figure 9. Sample pressure of 1.16 p.s.i.

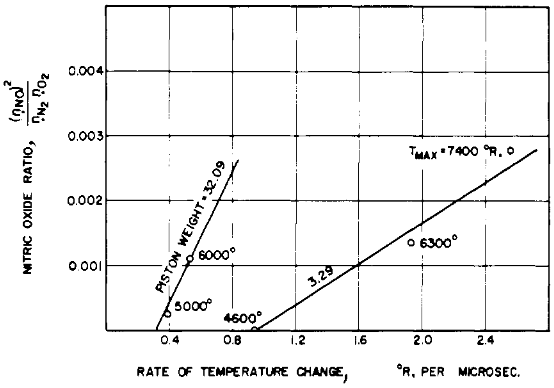

Figure 10. Sample pressure of 4.62 p.s.i.

Subscripts

e = condition corresponding to equilibrium
max = maximum

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