a_t = apparent turbulence level (fractional)
γ = mixture ratio, expressed as per cent combustibles relative to stoichiometric quantity required
σ = standard error of estimate

Subscripts

e = experimental value
m = smoothed value

Superscript

$\overline{\ }$ = time average

LITERATURE CITED

(1) Amell, A.R., Daniels, F., *J. Am. Chem. Soc.* **74**, 6209 (1952).
(2) Am. Soc. Testing Materials, Philadelphia, "Oxides of Nitrogen in Gaseous Combustion Products (Phenol-Disulfonic Acid Procedure)," ASTM Designation D 1608-58T, "1958 Book of ASTM Standards," Part 10, p. 1297, 1958.
(3) Beatty, R.L., Berger, L.B., Schrenk, H.H., Bur. Mines, Rept. Invest. **3687** (February 1943).
(4) Berry, V.J., Mason, D.M., Sage, B.H., *Ind. Eng. Chem.* **45**, 1596 (1953).
(5) Davis, Leo, "Measurements of Turbulence Level behind a Set of Square-Mesh Grids and Correlation with Grid Pressure Loss," Report 3-22, 1950; "Measurements of Turbulence Decay and Turbulent Spectra behind Grids," Report 3-17, 1952, Jet Propulsion Laboratory, California Institute of Technology, Pasadena.
(6) Grant, H.L., Nisbet, I.C.T., *J. Fluid Mechanics* **2**, 263 (1957).
(7) Hsu, N.T., Reamer, H.H., Sage, B.H., Am. Document Inst., Washington 25, D. C., Document **4219** (1954).
(8) Olin, J.B., Sage, B.H., J. CHEM. ENG. DATA **5**, 16 (1960).
(9) Reamer, H.H., Sage, B.H., *Rev. Sci. Instr.* **24**, 362 (1953).
(10) Richter, G.N., Wiese, H.C., Sage, B.H., Am. Document Inst., Washington 25, D. C., Document 6661 (1960).
(11) Richter, G.N., Wiese, H.C., Sage, B.H., unpublished data.
(12) Shenker, Harry, Lauritzen, J.I., Jr., Corruccini, R.J., Lonberger, S.T., "Reference Tables for Thermocouples," Natl. Bur. Standards Circ. **561** (April 27, 1955).
(13) Spindt, R.S., Wolfe, C.L., Stevens, D.R., *J. Air Pollution Control Assoc.* **6**, 123 (1956).

RECEIVED for review February 19, 1960. Accepted November 21, 1960. Material supplementary to this article has been deposited as Document No. 6661 with the ADI Auxiliary Publications Project, Photoduplication Service, Libary of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting \$3.75 for photoprints or \$2.00 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to Chief, Photoduplication Service, Library of Congress.

Thermal Decomposition and Partial Oxidation of Ammonia

J. B. OLIN and B. H. SAGE
Chemical Engineering Laboratory, California Institute of Technology, Pasadena, Calif.

THE PRESENT STUDY was stimulated in part by reports in the Russian literature (*2, 4, 9, 12*) of the synthesis of ammonia at high pressures and temperatures in a ballistic piston apparatus. It appeared that some low-entropy hydrogen-nitrogen compounds, such as hydrazine (*1, 3*), might be obtained as secondary products from the synthesis of ammonia. It was desired also to study the thermal decomposition and partial oxidation of ammonia as a possible approach to the formation of such products. The present investigation was carried out in a ballistic piston apparatus (*5, 6*) at maximum apparent pressures as high as 97,000 p.s.i.a. and maximum apparent temperatures up to 15,000° R.

EXPERIMENTAL APPROACH

The ballistic piston apparatus has been described in detail (*5, 6*). A cylinder, 3 inches in inside diameter and 11 feet long, surrounds a free piston. A space below the piston confines the sample, and a space above it contains the driving air. When a shear pin which restrains the piston is broken, the downward motion of the piston rapidly compresses the sample. The position of the piston as a function of time is measured with electrical contacts, four of which are located along the wall of the cylinder and four in the bottom face of the cylinder. After the sample reaches a minimum volume, the piston is accelerated upward, and the sample rapidly expands. The entire apparatus is constructed of low-carbon steel.

The sample was prepared by introducing the necessary amount of each component to the space below the piston. The initial composition was computed from temperature and pressure measurements obtained during the introduction. After compression and expansion, a sample of the product was withdrawn and its composition determined by mass spectrographic analysis. Samples were introduced and withdrawn using conventional high vacuum techniques. In the course of each test, the driving gas pressure, the sample pressure, and the position of the piston as a function of time were determined.

The experimental technique has been described (*5, 6*). It is believed that uncertainties in the analyses did not contribute significant errors in interpretation of the results. The volumetric compression ratio was known with an uncertainty of approximately 0.2%, and the position-time relationship of the piston was established within 0.002 inch and 2 microseconds.

From the basic experimental measurements, the maximum apparent pressure and maximum apparent temperature in the sample were determined, assuming that the gas was compressed isentropically from its initial volume to its minimum volume, returning then to a standard isentropic state. The influence of variation in composition of the system with time was not taken into account in calculating apparent pressure and apparent temperature. Some significant deviation of the apparent values of pressure and temperature from those actually realized is to be expected, particularly in cases in which appreciable

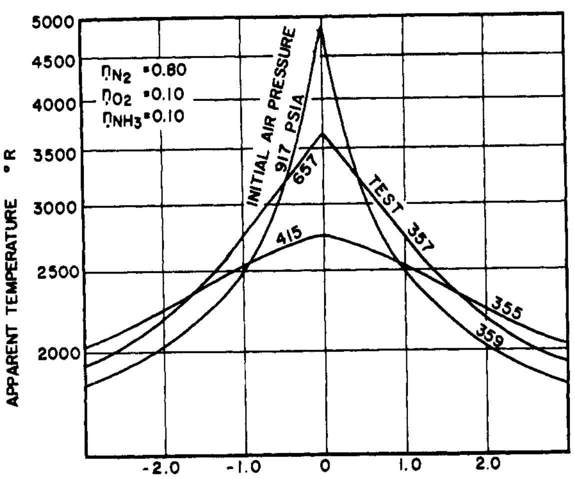

Figure 1. Apparent temperature-time relations using piston weighing 32.04 pounds

chemical reaction took place. A detailed description of these calculations is available (*7*).

As an illustration of the apparent temperatures realized in the ballistic piston apparatus, the behavior of mixtures of nitrogen, oxygen, and ammonia is shown in Figure 1, assuming isentropic compression and expansion and no chemical reaction. The effect of change in the driving air pressure upon the behavior of the system is evident. The apparent temperatures presented in Figure 1 were computed, but are in fair agreement with limited experimental data. Figure 2 depicts the computed variation in apparent pressure ratio with apparent temperature for several typical mixtures. This ratio is defined as the quotient of the apparent pressure of the sample at the state of interest and the initial pressure of the sample.

MATERIALS

The ammonia was obtained from commercial sources and was reported to contain less than 0.001 mole fraction of material other than ammonia. This was confirmed by spectrographic analysis. The nitrogen was obtained from

Table I. Experimental Conditions

	Initial Conditions[a]		Conditions at Minimum Volume[b]				
Test No.	Air pressure, p.s.i.a.	Sample pressure, p.s.i.a.	Piston approach, inches	Volumetric compression ratio	Max. apparent temp., °R.	Max. apparent pressure, p.s.i.a.	Max. apparent pressure ratio
			Formation of Ammonia				
56	999.1	1.9029	0.0341	3227	7,800	66,000	34,700
59	999.0	1.8268	0.0679	1557	>15,000	>55,000	>30,000
85	1017.4	2.4916	0.0446	2385	7,300	64,000	25,700
88	1017.4	2.5014	0.0457	2323	7,300	64,300	25,700
89	1016.4	2.5032	0.0308	3562	8,000	97,100	38,800
91	899.6	2.8878	0.2378	427	8,100	17,600	6,100
94	897.1	2.8799	0.2197	467	8,400	19,900	6,900
109	900.3	2.8882	0.2382	430	8,100	17,600	6,100
			Thermal Rearrangement of Ammonia				
106	876.7	2.5054	0.1659	629	8,100	21,500	8,600
456	233.0	2.8765	0.5069	197	1,800	1,700	600
457	371.4	2.8765	0.0441	1770	2,600	25,600	8,900
458	166.5	2.8712	1.9250	54	1,400	330	110
459	330.5	2.8683	0.0757	1138	2,400	13,600	4,800
			Partial Oxidation of Ammonia				
346	388.6	2.8779	0.5175	195	3,300	3,200	1,100
347	606.1	2.8749	0.2147	462	4,300	10,000	3,500
349	805.0	2.8806	0.0853	1081	5,500	31,100	10,800
351	961.3	2.8784	0.0723	1252	5,800	40,000	13,900
353	1085.4	2.8944	0.0608	1465	6,000	46,900	16,200
355	415.1	2.8696	0.7294	136	2,800	2,000	700
357	657.1	3.0642	0.2545	381	3,700	8,300	2,700
359	917.5	2.8732	0.0715	1273	5,000	33,900	11,800
365	657.2	2.8792	0.2221	446	3,800	8,900	3,100
375	1002.1	3.0710	0.0578	1577	5,300	48,200	15,700
377	1166.9	2.8809	<0.0448	>1984	>5,600	>60,000	>20,800
368	350.8	2.8306	>1.03	<96	<4,900	<2,500	<900
370	209.5	2.8783	>2.16	<46	<3,500	<860	<300
460	230.0	2.8767	0.6280	159	1,800	1,600	560
463	350.9	2.8770	0.0884	1035	2,400	1,300	440
464	161.3	2.8639	2.3836	44	1,400	320	110
465	442.8	2.8885	0.0432	1934	2,700	30,600	10,600
466	238.2	2.8949	0.6510	153	1,800	1,400	470
467	391.7	2.8645	0.1240	754	2,500	11,100	3,900
468	253.6	2.8710	0.5868	171	1,900	1,800	620
469	166.5	2.8900	1.250	90	1,800	1,300	440
471	146.0	2.8748	3.403	30	1,300	180	62
474	171.5	2.8767	2.3442	45	2,000	490	170
475	412.1	2.8787	0.4948	203	3,100	3,500	1,200
476	186.9	2.8814	2.4771	42	2,000	430	150
477	779.6	2.8701	0.1504	664	4,000	12,800	4,450
478	258.7	2.8718	0.7648	136	2,600	1,800	630
479	161.3	2.8737	1.6839	64	1,500	480	170

[a] Piston weight 3.28 pounds for test 478 and 479; 30.97 pounds for tests 56–109; 32.04 for remainder of tests. Initial sample volume, approximately 0.428 cu. ft. for tests 478 and 479, approximately 0.407 cu. ft. for remainder of tests. [b] Closest piston approach measured with lead crusher gage.

Linde Air Products Co., and was reported to contain only trace quantities of argon. The oxygen was also obtained from Linde and was reported to contain less than 0.002 mole fraction of material other than oxygen. The helium, obtained from commercial sources, did not contain more than 0.005 mole fraction of impurities. It is believed that the purity of all the gases employed in the investigation was adequate for such a study. Trace components which were reported in some of the mass spectrographic analyses of the products resulted from the presence of impurities in the initial sample and were disregarded in considering the results.

EXPERIMENTAL RESULTS

All the experimental conditions of the studies concerning the formation, thermal rearrangement, and partial oxidation of ammonia are set forth in Table I. The volumetric compression ratio is defined as the ratio of the initial volume to the minimum volume of the sample. The maximum apparent pressure ratio is the ratio of the maximum apparent pressure reached by the sample to the initial pressure of the sample, for an isentropic change in volume at constant composition.

The specific volume of several samples is shown in Figure 3 as a function of time. In arriving at these data, the small leakage past the piston during the rapid compression was neglected.

Tables II and III record the initial and final compositions of each sample.

Synthesis of Hydrogen-Nitrogen Compounds. It was not possible under any of the conditions encountered, including

Table II. Initial Composition of Samples

Test No.	He	H_2	NH_3	N_2	O_2
		Formation of Ammonia			
56	...	0.6670	...	0.3330	...
59	0.6666[a]	0.2218	...	0.1116	...
85	...	0.6675	...	0.3325	...
88[b]	...	0.6666	...	0.3334	...
89[c]	...	0.6319	...	0.3222	...
91	0.5002	0.3326	...	0.1672	...
94[d]	0.4998	0.3340	...	0.1662	...
109[e]	0.4900	0.3267	...	0.1634	...
		Thermal Rearrangement of Ammonia			
106	0.8229	...	0.1771	...	...
456	...	...	1.0000	...	...
457	...	...	1.0000	...	...
458	...	...	1.0000	...	...
459	...	...	1.0000	...	...
		Partial Oxidation of Ammonia			
346	...	...	0.0101	0.8857	0.1042
347	...	...	0.0104	0.8937	0.0959
349	...	...	0.0122	0.8978	0.0900
351	...	...	0.0139	0.8866	0.0995
353	...	...	0.0105	0.8911	0.0984
355	...	...	0.0997	0.8000	0.1003
357	...	...	0.0973	0.7978	0.1049
359	...	...	0.1097	0.8021	0.0882
365	...	...	0.0980	0.8011	0.1009
375	...	...	0.0993	0.7988	0.1019
377	...	...	0.0995	0.7990	0.1015
368	0.7992	...	0.0999	...	0.1009
370	0.8001	...	0.1008	...	0.0991
460	...	...	0.9492	...	0.0508
463	...	...	0.9500	...	0.0500
464	...	...	0.9501	...	0.0499
465	...	...	0.9500	...	0.0500
466	...	...	0.9000	...	0.1000
467	...	...	0.8001	...	0.1999
468	...	...	0.8004	...	0.1996
469	...	...	0.7998	...	0.2002
471	...	...	0.8000	...	0.2000
474	0.5010	...	0.4491	...	0.0499
475	0.5023	...	0.3979	...	0.0998
476	0.5063	...	0.3954	...	0.0983
477	0.4974	...	0.4020	...	0.1006
478	0.4960	...	0.4537	...	0.0503
479	...	...	0.9500	...	0.0500

Initial compositions computed from temperature and pressure measurements obtained during introduction of samples, reported in mole fraction. [b] Ferric oxide used as catalyst. [c] Iron carbonyl used as catalyst. [d] Mixture of ferric and ferrous oxides used as catalyst. [e] Approximately 0.02 mole fraction water introduced in sample.

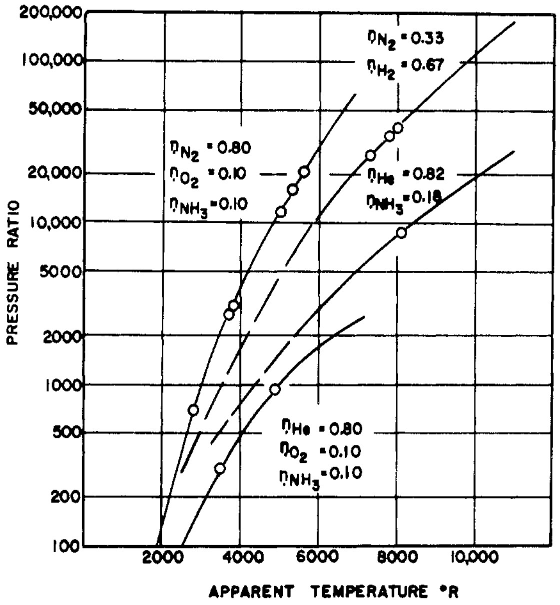

Figure 2. Range of pressure ratios and apparent temperatures

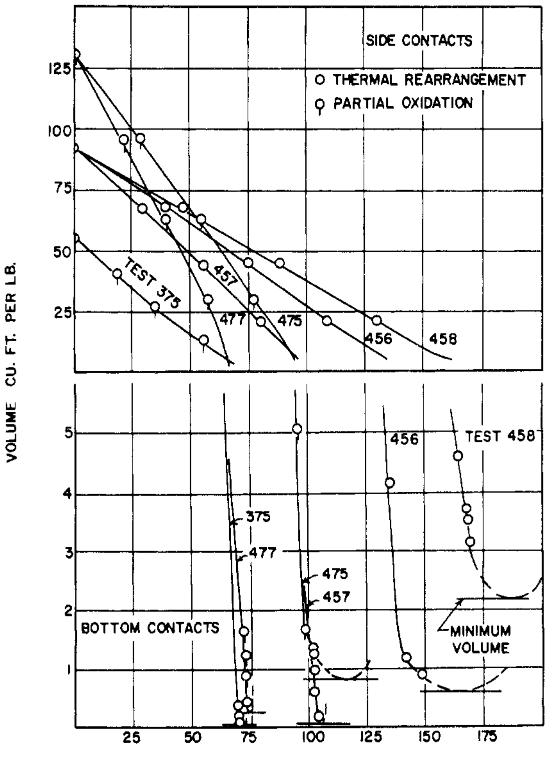

Figure 3. Specific volume as a function of time

pressures as high as 97,000 p.s.i.a. and apparent temperatures greater than 15,000° R., to obtain any measurable amount of ammonia or other hydrogen-nitrogen compounds from initial mixtures of hydrogen and nitrogen. The authors are at a loss to explain the information presented by Tsiklis (*12*) and others (*2, 4, 9*). The absence of hydrazine lends strong credence to the thermodynamic predictions of Parts (*8*) and Scott (*10*). The negative results obtained for the synthesis of hydrogen-nitrogen compounds at elevated pressures and temperatures in the ballistic piston are not unexpected in view of the kinetics of these reactions (*4, 11*) as they are now known.

Thermal Rearrangement of Ammonia. The limited experimental information obtained from study of the thermal rearrangement of ammonia is set forth in Table IV. In the absence of a diluent, no significant thermal decomposition of ammonia occurred at apparent temperatures as high as 2600° R. and maximum apparent pressures as high as 25,000 p.s.i.a. When the ammonia was diluted with approximately 0.82 mole fraction helium, however, about 96% of the ammonia decomposed into hydrogen and nitrogen at a maximum apparent temperature of 8100° R. and a pressure of only 21,500 p.s.i.a. This difference in the thermal rearrangement of pure ammonia and ammonia in the presence of a diluent is marked and appears to indicate that the maximum apparent temperature is of much greater significance in inducing the thermal rearrangement of ammonia than any other factor. Attempts to reach high apparent temperatures by compression of ammonia alone were not effective (Table I).

Partial Oxidation of Ammonia. Studies of the partial oxidation of ammonia carried out on mixtures of ammonia and oxygen, with and without inactive diluents, are reported in Table IV. When the molal ratio of ammonia to oxygen was larger than stoichiometric, an excess of ammonia remained for thermal rearrangement, even though the oxidation reaction was carried to completion. The fraction completion of the oxidation reaction was the same as the fraction of initial ammonia oxidized when the extent of the oxidation was controlled by the mole fraction of ammonia, but was different when the extent of the oxidation was controlled by the mole fraction of oxygen. The total of the mole fraction of ammonia oxidized and the mole fraction of ammonia rearranged amounted to the mole

Table III. Final Composition of Samples

Test No.	He	H_2	NH_3	N_2	O_2	H_2O	Ar	CO	CO_2	NO_2	Air	Hydrocarbon[b]
						Formation of Ammonia						
56	...	0.6692	...	0.3275	0.0003	0.0009	...	...	0.0002	...	...	0.0019
59	0.6791[a]	0.2036	...	0.1116	0.0003	0.0021	...	...	0.0002	0.0013[c]	...	0.0018
85	...	0.6628	...	0.3281	...	0.0053	...	...	...	...	0.0016	0.0022
88	...	0.6418	...	0.3440	...	0.0125	0.0001	...	...	...	...	0.0016
89	...	0.4449	...	0.3017	0.0024	0.0147	...	0.0866[d]	0.0013	...	...	0.1484[d]
91	0.4999	0.3329	...	0.1629	...	0.0028	0.0002	...	...	...	...	0.0016
94	0.5182	0.3142	...	0.1626	...	0.0041	0.0001	...	...	...	...	0.0008
109	0.4976	0.3297	...	0.1699	...	0.0001	...	...	...	...	0.0010	...
						Thermal Rearrangement of Ammonia						
106	0.7230	0.2005	0.0063	0.0649	...	0.0027	...	...	...	...	0.0020	0.0006
456	...	...	0.9728	...	...	0.0272	...	...	...	...	...	...
457	...	...	0.9714	...	...	0.0286	...	...	...	...	...	...
458	...	...	0.9784	...	...	0.0216	...	...	...	...	...	...
459	...	...	0.9746	...	...	0.0254	...	...	...	...	...	...
						Partial Oxidation of Ammonia						
346	...	...	0.0009	0.8639	0.1073	0.0240	0.0024	...	0.0015	...	...	...
347	...	...	0.0008	0.8917	0.0985	0.0065	0.0004	...	0.0021	...	...	...
349	...	...	0.0027	0.9076	0.0709	0.0019	0.0004	...	0.0165	...	...	...
351	...	...	0.0002	0.9038	0.0835	0.0081	0.0004	...	0.0040	...	...	...
353	...	...	0.0010	0.8607	0.1056	0.0137	0.0004	...	0.0186	...	...	...
355	...	...	0.0002	0.9495	0.0394	0.0072	0.0002	...	0.0035	...	...	...
357	...	...	0.0002	0.9767	0.0137	0.0024	0.0004	...	0.0066	...	...	...
359	...	0.0069	0.0027	0.9658	0.0006	0.0060	0.0004	0.0064	0.0108	...	...	...
365	...	...	0.0002	0.9755	0.0167	0.0030	0.0004	...	0.0042	...	...	...
375	...	...	0.0008	0.8763	0.0476	0.0064	0.0008	...	0.0681[e]	...	...	...
377	...	0.0192	0.0004	0.9098	0.0017	0.0066	0.0006	0.0303[e]	0.0293[e]	...	...	0.0021
368	0.8992	...	0.0008	0.0651	0.0289	0.0048	0.0004	...	0.0008	...	...	...
370	0.8460	...	0.0145	0.0128	0.1145	0.0114	0.0004	...	0.0004	...	...	...
460	...	...	0.9270	...	0.0469	0.0261	...	...	...	...	...	...
463	...	0.0234	0.8991	0.0359	0.0132	0.0284	...	...	...	...	...	...
464	...	...	0.9224	...	0.0454	0.0318	...	...	...	0.0004[c]	...	...
465	...	0.0146	0.9002	0.0377	0.0186	0.0289	...	...	...	...	...	...
466	...	0.0023	0.8663	0.0064	0.0792	0.0458	...	...	...	...	...	...
467	...	0.5928	0.1175	0.3120	0.0038	0.0365	0.0004	...	...	...	...	...
468	...	0.5440	0.1298	0.2972	0.0033	0.0253	0.0004	...	...	...	...	...
469	...	0.5309	0.1268	0.3114	0.0014	0.0291	0.0004	...	...	...	...	...
471	...	...	0.7716	...	0.2040	0.0232	0.0004	...	...	0.0008	...	...
474	0.4855	...	0.4331	...	0.0449	0.0365	...	...	...	...	...	...
475	0.4589	0.3182	0.0314	0.1605	0.0025	0.0283	0.0002	...	...	...	...	...
476	0.4756	...	0.3905	...	0.0860	0.0473	0.0002	...	...	0.0004	...	...
477	0.4321	0.3473	0.0267	0.1683	0.0028	0.0228	...	...	...	...	...	...
478	0.4922	0.0384	0.3633	0.0418	0.0046	0.0597	...	...	...	...	...	...
479	...	...	0.9311	...	0.0468	0.0221	...	...	...	...	...	...

[a] Compositions obtained by mass spectrographic analysis reported in mole fraction. [b] Hydrocarbon primarily methane. No trace of hydrogen cyanide. [c] Information concerning oxides of nitrogen subject to greater uncertainty than that for other components.

[d] Carbon monoxide and hydrocarbon apparently resulted from use of iron carbonyl as a catalyst. [e] Excessive quantities of graphite employed as lubricant caused formation of carbon monoxide and carbon dioxide.

Table IV. Thermal Rearrangement and Oxidation of Ammonia

	Initial Mixture		Product, Mole Fraction			
				Ammonia		
Test No.	Diluent,[a] mole fraction	Molal ratio, ammonia-oxygen	Completion of oxidation reaction	Oxidized	Rearranged	Total decomposed
			Thermal Rearrangement of Ammonia			
106	0.823	...	...	...	0.9595	0.9595
456	...	...	...	...	0.0000	0.0000
457	...	...	...	...	0.0000	0.0000
458	...	...	...	...	0.0000	0.0000
459	...	...	...	...	0.0000	0.0000
			Partial Oxidation of Ammonia			
346	0.886	0.097	0.908	0.908	0	0.9079
347	0.894	0.108	0.922	0.922	0	0.9221
349	0.898	0.136	0.780	0.780	0	0.7795
351	0.887	0.140	0.986	0.986	0	0.9856
353	0.891	0.107	0.901	0.901	0	0.9010
355	0.800	0.994	0.998	0.998	0	0.9982
357	0.798	0.928	0.998	0.998	0	0.9983
359	0.802	1.240	0.941	0.941	0.0372	0.9782
365	0.801	0.971	0.998	0.998	0	0.9983
375	0.799	0.974	0.992	0.992	0	0.9923
377	0.799	0.980	0.876	0.876	0.1203	0.9963
368	0.799	0.990	0.993	0.993	0	0.9929
370	0.800	1.017	0.864	0.864	0	0.8640
460	...	18.7	0.000	0.0000	0	0.0000
463	...	19.0	0.742	0.0520	0.0219	0.0740
464	...	19.0	0.000	0.0000	0	0.0004[b]
465	...	19.0	0.638	0.0478	0.0326	0.0773
466	...	9.00	0.189	0.0146	0	0.0146
467	...	4.00	0.979	0.3262	0.5153	0.8415
468	...	4.01	0.979	0.3254	0.4954	0.8208
469	...	4.00	0.993	0.3312	0.4997	0.8309
471	...	4.00	0.000	0.0000	0	0.0010[b]
474	0.501	9.00	0.000	0.0000	0	0.0000
475	0.502	3.99	0.973	0.3252	0.5884	0.9136
476	0.506	4.02	0.000	0.0000	0	0.0010[b]
477	0.497	4.00	0.968	0.3229	0.6007	0.9236
478	0.496	9.02	0.908	0.1342	0.0589	0.1931
479	...	19.0	0.000	0.0000	0	0.0000

[a] Mole fraction nitrogen or helium in initial mixture. For tests 346-377 diluent was nitrogen; for tests 106, 368, 370, and 472-478 diluent was helium. [b] Result of oxidation reaction in which oxides of nitrogen formed.

fraction of ammonia decomposed. In tests 359 and 377 some ammonia was thermally rearranged, even though the ammonia-oxygen molal ratio was less than stoichiometric.

The fraction of ammonia thermally rearranged, the fraction completion of the oxidation reaction, the fraction of initial ammonia which underwent oxidation, and the total fraction of ammonia decomposed are illustrated in Figure 4 as a function of time. The ammonia-oxygen molal ratio, ψ, is used as a parametric variable. With an increase in the ammonia-oxygen molal ratio, a higher maximum apparent temperature is required to introduce thermal rearrangement. This behavior is to be expected; the actual maximum temperature is much higher when the molal ratio of ammonia to oxygen is low than when it is high, because of the increased extent of the exothermic oxidation reaction at low ratios. In the presence of a diluent the rate of thermal rearrangement decreases. At an ammonia-oxygen molal ratio of 4, a temperature of 2000° R. is required to initiate thermal rearrangement in the presence of helium, whereas only about 1300° R. is required when no diluent is present.

Figure 4 shows a progressive increase in the maximum apparent temperature required to initiate the oxidation reaction with increase in the ammonia-oxygen molal ratio. It was not possible to investigate the maximum apparent temperature at which oxidation was initiated in the case of molal ratios below 4. For the same ammonia-oxygen molal ratio the presence of a diluent necessitates a higher maximum apparent temperature to initiate reaction. With large quantities of diluent and small quantities of ammonia the oxidation reaction did not proceed to completion, even at 6000° R.

When the ammonia-oxygen molal ratio was less than stoichiometric, it was possible for all the ammonia to be oxidized, and this was approached for all such mixtures, including those containing diluents. For ammonia-oxygen molal ratios greater than the stoichiometric value, the maximum fraction oxidized was controlled by the available oxygen. This accounts for the fact that the fraction of ammonia oxidized is independent of the maximum apparent temperature at the higher apparent temperatures. Again, for the lower ammonia-oxygen molal ratios the oxidation reaction is completed at a lower apparent temperature than for the higher values. Furthermore, the diluent has a pronounced effect on the maximum apparent temperature required to complete the oxidation reaction.

High ammonia-oxygen molal ratios require higher maximum apparent temperatures to induce a specific fractional decomposition of ammonia than low molal ratios, both with and without diluents.

Figure 4 shows the influence of diluents upon the rate of partial oxidation and thermal rearrangement of ammonia and illustrates the limitation of the maximum apparent temperature as an independent variable. Figure 5 shows the total fraction of ammonia decomposed as a function of volumetric compression ratio for the same parametric

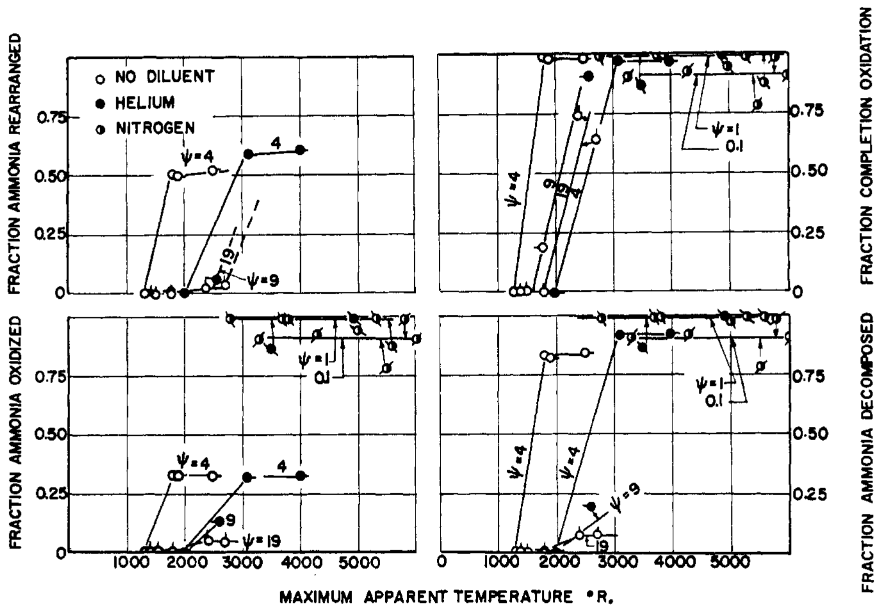

Figure 4. Effect of maximum apparent temperature on rearrangement and partial oxidation of ammonia

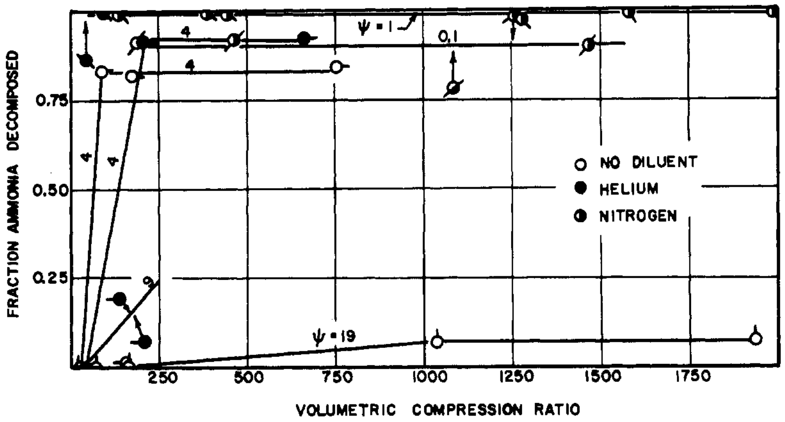

Figure 5. Fraction of ammonia decomposed as a function of volumetric compression ratio

variables as shown in Figure 4. The volumetric compression ratio required to obtain a certain fraction of total ammonia decomposed is higher at the higher ammonia-oxygen molal ratios and in the presence of a diluent.

ACKNOWLEDGMENT

The Montebello Laboratory, Texaco, Inc., made the mass spectrographic analyses reported. Harry Wiese did most of the experimental work, under the general direction of H.H. Reamer. Virginia Berry prepared the data in a form suitable for publication, and Ann Taylor contributed to preparation of the manuscript.

LITERATURE CITED

(1) Gedye, G.R., Rideal, E.K., *J. Chem. Soc.* **54**, 1160–9 (1932).
(2) Kiperman, S.L., Granovskaya, V. Sh., *Zhur. Fiz. Khim.* **26**, 1615–8 (1952).
(3) Kouzmine, E., French Patent **966,320** (Oct. 6, 1950).
(4) Livshits, V.D., Sidrov, I.P., *Zhur. Fiz. Khim.* **26**, 538–41 (1952).
(5) Longwell, P.A., "Chemical Reactions of Methane and of *n*-Hexane in Ballistic Piston Apparatus," Ph.D. thesis, California Institute of Technology, Pasadena, Calif., 1957.
(6) Longwell, P.A., Reamer, H.H., Wilburn, N.P., Sage, B.H., *Ind. Eng. Chem.* **50**, 603–10 (1958).
(7) Olin, J.B., Wiese, H., Sage, B.H., Supplementary Material to Article Entitled "Thermal Rearrangement of Methane, *n*-Butane, *n*-Hexane, and *n*-Octane in the Presence of Hydrogen," Am. Doc. Inst., Washington 25, D.C., Doc. 6662 (1961).
(8) Parts, A.G., *Ann. Univ. Ankara* **2**, 217–30 (1948).
(9) Ryabinin, Yu. N., *Zhur. Eksptl. Fiz.* **23**, 461–7 (1952).
(10) Scott, D.W., Oliver, G.D., Gross, M.E., Hubbard, W.N., Huffman, H.M., *J. Am. Chem Soc.* **71**, 2293–7 (1949).
(11) Temkin, M.I., Pyzhev, V., *Zhur. Fiz. Khim.* **13**, 851–67 (1939).
(12) Tisklis, D.S., *Doklady Akad. Nauk (U. S. S. R.)* **91**, 327–9 (1953).

RECEIVED for review April 18, 1960. Accepted November 21, 1960. Work carried out with financial support of Texaco, Inc.