Thermodynamic Properties of the Decomposition Products of Hydrazine

WILLIAM D. VAN VORST and R. C. AHLERT[1] University of California, Los Angeles, Calif.

Mollier-type diagrams are presented for the products of the decomposition of hydrazine for decomposition temperatures of 865°, 1163°, 1380°, 1534°, and 1646° K., over a pressure range of 1 to 100 atm. These temperatures correspond to ammonia concentrations in the products of 0, 20, 40, 60, and 80 mole per cent, respectively. The diagrams are the result of equilibrium computations, considering NH_3, N_2, and H_2 to be present after the decomposition.

CONSIDERABLE CURRENT interest in hydrazine is centered about its application as a fuel. It reacts satisfactorily with a variety of oxidizers to furnish bipropellent combinations for use in rocket engines. In such combinations, it also forms a highly acceptable source of gas generation for turbo drive mechanisms.

In addition to its use as a bipropellent, it may also serve as a monopropellent—i.e., the energy release and the products of its own decomposition are satisfactory for use in rocket engines and gas generators.

While this interest has resulted in the generation and publication of much information on the general properties of hydrazine (*1*), properties of its decomposition products are not so readily available. [Lucien (*5*) has studied the thermal decomposition per se; his emphasis, however, is on rate rather than products of decomposition.] Accordingly, computations were undertaken to obtain the properties of particular interest in evaluating the performance of devices employing hydrazine as a monopropellent. The most recent information available in the open literature was employed in the computations, and though one suspects rather more is available in the classified literature, the results reported here are considered to be the most satisfactory generally available.

METHODS AND DATA EMPLOYED

The bulk of the products of the homogeneous decomposition of hydrazine consists of ammonia, nitrogen, and hydrogen and it is postulated that severe inaccuracies will not result from considering these to be the only products. Thus the decomposition of hydrazine may be represented by:

$$3N_2H_4 \rightarrow 4(1-x)NH_3 + (1+2x)N_2 + 6xH_2 \qquad (1)$$

where x is the "reaction variable" defined by Equation 1. The method of computation is implicit in the equation: First, a compilation of the thermal properties of the products over the temperature range of interest is indicated; second, the determination of x as a function of reaction temperature; and third, presentation of the averaged properties of the product gas as a function of temperature and pressure.

The heat capacity data of Huff, Gordon, and Morrell (*4*), and of Harrison and Kobe (*3*) were chosen as the basis of the necessary compilation of thermodynamic properties of hydrogen (*4*), nitrogen (*4*), and ammonia (*3*). These data are from spectroscopic measurements; equations of the form $C_p = d + eT + fT^2$ were fitted to the data over various temperature ranges chosen so that the deviation of the curve from the equation was tolerable. The average deviations were 0.07, 0.015, and 0.01 per cent for ammonia, hydrogen, and nitrogen, while the maximum deviations were 0.22, 0.03, and 0.04 per cent, respectively. As indicated by these deviations, the heat capacities of ammonia are the least accurate; moreover, they have been extrapolated beyond the range given by Harrison and Kobe. This results in increasing uncertainty in the upper portion of the temperature range, though it is felt that the accuracy is sufficient for the purposes of this work. Selected values of the properties are presented in Table I. A temperature of 298.2° K. and a pressure of 1 atm. was chosen as the reference state. An upper limit of 1700° K. was chosen since exploratory computations indicate a maximum decomposition temperature in the neighborhood of 1600° K. Values of the enthalpy and entropy above the reference state were obtained by appropriate treatment of the general equations:

$$dH = C_p\,dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]dP \qquad (2)$$

$$dS = C_p\frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP \qquad (3)$$

(Note: Equation 2 becomes $dH = C_p\,dT$,

and Equation 3, $dS = C_p\frac{dT}{T} - R\frac{dP}{P}$ for the ideal gas.)

First, values of the heat capacities of the individual gases were obtained at various temperatures and one atmosphere; these are presented in Table I. Second, the effect of pressure of the heat capacity, enthalpy, and entropy of the individual gases was estimated at the temperatures of Table I; differences in these properties at one atmosphere and at pressures of 25, 50, 75, and 100 atm. are tabulated in Table II. In estimating the effect of pressure on heat capacity, enthalpy, and entropy, a Beattie-Bridgeman equation was developed for each gas, and used to obtain explicit relations for the quantities of interest. Though cumbersome, it seems less subject to error than graphical differentiation. The values used for the constants were those suggested by Beattie (*6*). The results of these calculations are presented in Table II. These values, together with the values of Table I yield values of the heat capacity, enthalpy, and entropy at various temperatures. In the case of the entropy one must add the "ideal" effect of pressure; $R \ln P_2/P_1$, as indicated in the note following Equations 2 and 3. For example, at 75 atmospheres and 1100° K., the heat capacity of ammonia is (14.021 + 0.151); the enthalpy is (9064 − 60.22) and entropy is (13.977 + 8.574), the zero datum of the latter two being 298.2° K. The figure 8.574 is the pressure effect on the ideal gas, $R \ln 75$; $R = 1.986$ cals./(gram mole) (° K.). These properties in turn may be averaged to give properties of the gaseous mixtures implied by Equation 1. In estimating the average properties, the rule of Lewis and Randall was employed (*7*). The final results are presented as a series of Mollier diagrams each for a different percentage of ammonia in the decomposition products (Figures 1, 2, 3, 4, and 5).

Values of the reaction variable x were calculated as a function of the decomposition by means of the usual flame temperature energy balance which in this case may be written

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[1] Present address: Rocketdyne, Canoga Park, Calif.

$$\sum_i \int_{T=298.2}^{T=T_f} n_i\, C_{pi}\, dT = -26{,}613 + 14{,}613\,x \qquad (4)$$

where the subscript f indicates flame conditions, and i simply indicates nitrogen, hydrogen, and ammonia. The left hand side of the equation is the total sensible enthalpy of the products of the decomposition above the reference state, while the right hand member gives the energy released by the decomposition reaction at the reference state. This latter energy is, of course, the heat of reaction, which from Equation 1 may be written in terms of heats of formation of hydrazine and ammonia:

$$\Delta H_R = 4\,(1 - x)\Delta H_{F-\mathrm{NH_3}} - 3\Delta H_{F-\mathrm{N_2H_4}}$$

Using values of −10,960 and 12,000 cal./gram mole for ammonia and hydrazine respectively, one obtains Equation 4. In making the computations, the equations obtained from the heat capacity data (*2*) and (*3*) were used, resulting in a final equation in which T_f and x appear explicitly. One need only choose several values of T_f and solve for the corresponding x's to get the desired relation. There are two items of concern in this computation. First, there seems to be less certainty of the value of the heat of formation of hydrazine than of the great majority of compounds. Audrieth and Ogg (*2*) recommend the value of 12,000 though noting other results. If the value of 12,000 were off by 100, computations indicate a resulting difference of 4° K. in the flame temperature estimate. This may be ruled a tolerable degree of uncertainty. The second item

Table I. Some Heat Capacities in the Ideal Gas State

Temp., ° K.	Heat Capacity, Cal./Gram Mole, ° K. Ammonia	Hydrogen	Nitrogen
273.2	8.371	...	...
298.2	8.514	6.892	6.960
300	8.526	6.895	6.961
400	9.241	6.974	6.991
500	10.036	6.993	7.070
600	10.808	7.008	7.197
700	11.538	7.035	7.351
800	12.225	7.078	7.512
900	12.868	7.139	7.671
1000	13.467	7.219	7.816
1100	14.021	7.310	7.947
1200	14.530	7.407	8.063
1300	14.994	7.509	8.165
1400	15.414	7.615	8.253
1500	15.791	7.720	8.330
1600	16.122[a]	7.823	8.399
1700	16.409[a]	7.923	8.459

[a] Extrapolated values.

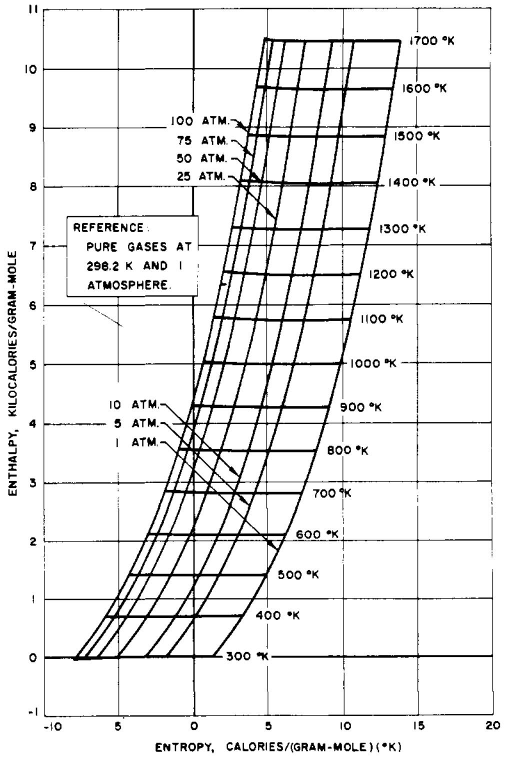

Figure 1. Enthalpy-entropy diagrams for hydrazine decomposition products containing 0 mole per cent ammonia (x = 1).

(Decomposition temperature 865° K.)

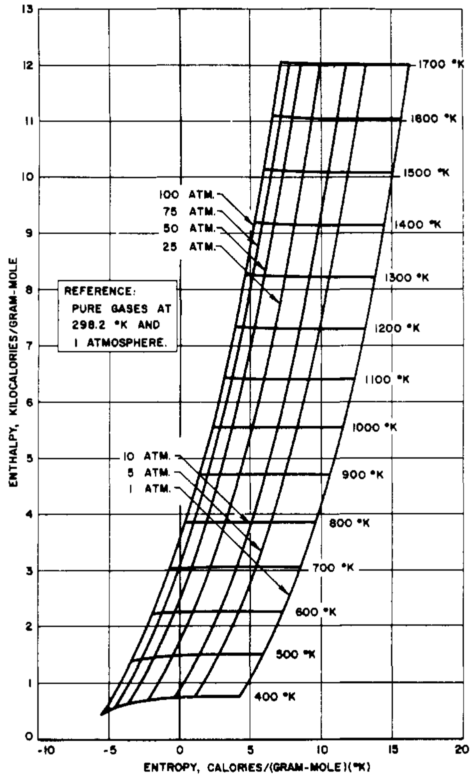

Figure 2. Enthalpy-entropy diagram of hydrazine decomposition products containing 20 mole per cent ammonia (x = 0.625).

(Decomposition temperature 1163° K.)

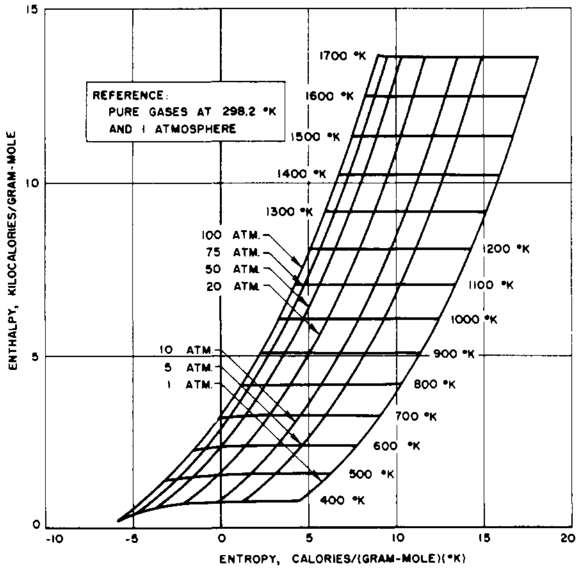

Figure 3. Enthalpy-entropy diagram for hydrazine decomposition products containing 40 mole per cent ammonia (x = 0.359).

(Decomposition temperature 1380° K.)

Table II. Thermodynamic Properties of NH_3, N_2, and H_2 at Various Pressures and Temperatures

Temp., ° K.	At Pressures of:				At Pressures of:				At Pressures of:			
	25 atm.	50 atm.	75 atm.	100 atm.	25 atm.	50 atm.	75 atm.	100 atm.	25 atm.	50 atm.	75 atm.	100 atm.
	$(C_p - C_p^*)_T$, Cal./Gram Mole)(° K.)				$(H_p - H^*)_T$, Cal./Gram Mole)				$(S_p - S_p^*)_T$, Cal./(Gram Mole)(° K.)			
					Ammonia							
400	1.992	5.490	12.672	19.972	-269.50	-609.30	-1022.61	-1508.75	-0.4964	-1.1279	-1.9803	-2.9754
450	1.172	2.739	4.845	7.428	-193.11	-410.91	-638.48	-887.81	-0.3143	-0.6693	-1.0670	-1.4983
500	0.759	1.656	2.706	3.901	-145.79	-300.59	-457.77	-619.66	-0.2157	-0.4410	-0.6844	-1.0831
700	0.218	0.441	0.663	0.884	-63.22	-126.69	-187.80	-248.75	-0.0717	-0.1426	-0.2122	-0.2804
900	0.096	0.188	0.280	0.369	-34.34	-68.28	-101.41	-134.32	-0.0346	-0.0683	-0.1018	-0.1344
1100	0.052	0.102	0.151	0.199	-19.95	-40.32	-60.22	-80.32	-0.0203	-0.0402	-0.0599	-0.0792
1300	0.032	0.065	0.095	0.125	-11.99	-24.07	-36.20	-48.96	-0.0133	-0.0264	-0.0396	-0.0530
1500	0.022	0.044	0.066	0.086	-6.44	-13.34	-20.53	-28.02	-0.0097	-0.0187	-0.0285	-0.0380
1700	0.017	0.033	0.049	0.063	-2.62	-5.64	-9.42	-13.37	-0.0070	-0.0143	-0.0217	-0.0285
					Hydrogen							
400	0.031	0.058	0.082	0.104	3.42	7.65	12.71	18.48	-0.0153	-0.0295	-0.0421	-0.0530
450	0.017	0.035	0.047	0.059	5.72	12.03	18.96	26.32	-0.0087	-0.0165	-0.0237	-0.0300
500	0.011	0.021	0.030	0.039	7.11	14.67	22.69	31.04	-0.0058	-0.0104	-0.0155	-0.0194
700	0.006	0.011	0.016	0.020	8.67	17.70	27.02	36.56	-0.0029	-0.0056	-0.0079	-0.0101
900	0.004	0.006	0.010	0.012	9.64	19.40	29.42	39.64	-0.0017	-0.0033	-0.0048	-0.0063
1100	0.003	0.005	0.007	0.008	10.14	20.51	30.97	41.65	-0.0012	-0.0021	-0.0036	-0.0041
1300	0.002	0.004	0.005	0.006	10.56	21.16	32.08	43.00	-0.0008	-0.0017	-0.0024	-0.0026
1500	0.001	0.003	0.004	0.005	10.90	21.74	32.83	44.09	-0.0006	-0.0012	-0.0019	-0.0022
1700	0.001	0.002	0.003	0.004	11.20	22.20	33.42	44.80	-0.0005	-0.0007	-0.0017	-0.0017
					Nitrogen							
400	0.258	0.512	0.752	1.372	-38.09	-73.56	-105.50	-134.29	-0.1174	-0.2290	-0.3329	-0.4295
450	0.132	0.256	0.372	0.477	-19.64	-47.65	-52.96	-66.69	-0.0632	-0.1230	-0.1789	-0.2317
500	0.082	0.158	0.228	0.293	-9.25	-17.27	-23.90	-30.07	-0.0399	-0.0779	-0.1138	-0.1516
700	0.041	0.080	0.114	0.149	+2.30	+4.87	+8.31	+12.06	-0.0201	-0.0397	-0.0586	-0.0765
900	0.025	0.050	0.070	0.091	8.43	17.12	26.03	35.18	-0.0123	-0.0240	-0.0356	-0.0453
1100	0.018	0.031	0.047	0.062	12.62	24.99	37.63	50.22	-0.0082	-0.0160	-0.0242	-0.0322
1300	0.014	0.023	0.034	0.045	15.28	30.41	45.55	60.73	-0.0058	-0.0116	-0.0177	-0.0230
1500	0.011	0.016	0.025	0.034	17.12	34.48	51.48	68.45	-0.0043	-0.0087	-0.0133	-0.0172
1700	0.007	0.013	0.020	0.027	18.72	37.60	56.08	74.51	-0.0036	-0.0068	-0.0104	-0.0135

of interest is the effect of pressure on the flame temperature. Since earlier discussion has stressed the effect of pressure on C_p, one is naturally concerned with the effect in this calculation. It will be noted, however, from Table II that the magnitude of the effect diminishes rapidly with increasing temperature. Introduction of this effect in the computation does not change the result sufficiently to merit concern in view of the 4° K. uncertainty just described. Therefore, the effect of pressure was neglected in obtaining T_f *vs.* x. The relation of the flame temperature and the reaction variable is shown in Figure 6; for convenience x has been converted to per cent of ammonia in the products. The relationship between the average molecular weight and the temperature has also been included.

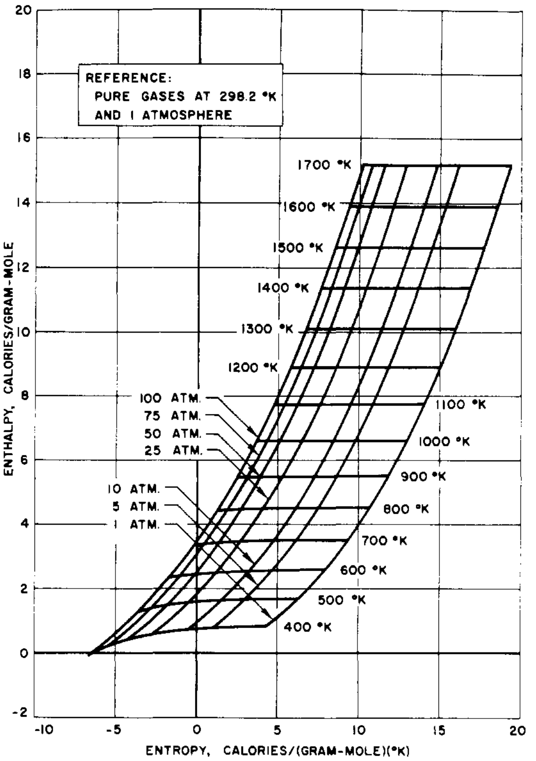

Figure 4. Enthalpy-entropy diagram for hydrazine decomposition products containing 60 mole per cent ammonia (x = 0.156).

(Decomposition temperature 1534° K.)

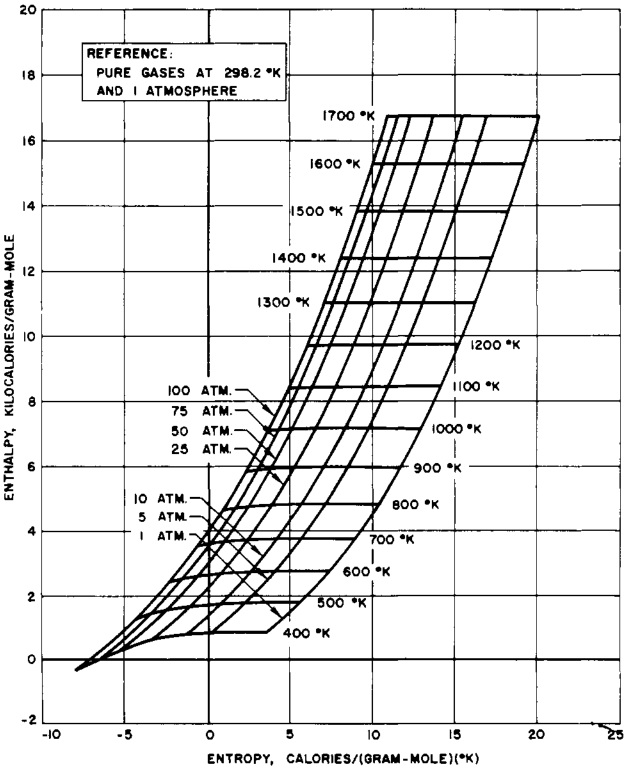

Figure 5. Enthalpy-entropy diagram for hydrazine decomposition products containing 80 mole per cent ammonia (x = 0).

(Decomposition temperature 1646° K.)

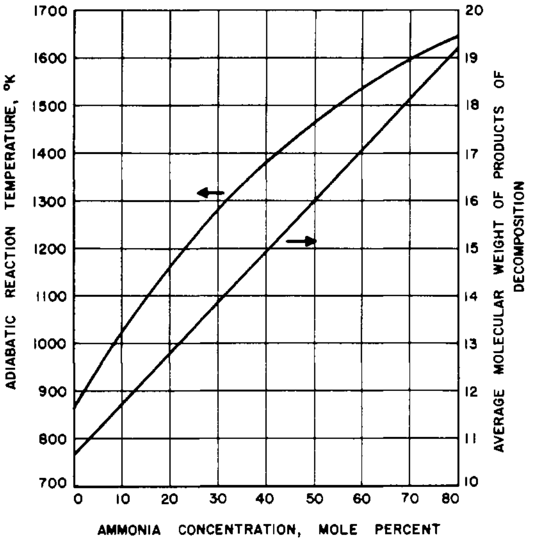

Figure 6. Adiabatic reaction temperature and average molecular weight of the products of the hydrazine decomposition reactions

NOMENCLATURE

C_p = heat capacity, at constant pressure cal./gram mole (° K.)
d = constant of heat capacity equation
e = constant of heat capacity equation
f = constant of heat capacity equation
H = enthalpy, cal./gram mole
ΔH_f = heat of formation, cal./gram mole
n = number of moles
P = press., atm.
S = entropy, cal./gram mole (° K.)
T = temp., ° K.
V = vol., liters
x = reaction variable.

Subscripts

b = base, or reference condition
f = flame temperature
i = property of component i
p = condition of constant pressure

Superscripts

$*$ = property in ideal gas state

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