EQUILIBRIA IN THE SYSTEM $2N_2 + H_2$ AND $N_2 + 8H_2$, AND THERMODYNAMIC PROPERTIES OF N_2H_4 AT 1000° TO 5000°K

Chikara Hirayama and Anthony M. DeRoo
Westinghouse Research & Development Center
Pittsburgh, Pennsylvania 15235

Although high temperature equilibrium data on systems containing carbon, hydrogen, and nitrogen have been reported, the same type of data for the more simple system containing hydrogen and nitrogen[1] have not been reported. Both systems are of obvious interest in the chemistry of reactions in a high-temperature plasma.

We presently consider the equilibria in the systems $2N_2 + H_2$ and $N_2 + 8H_2$ at 1000° to 5000°K. Ideal gas behavior is assumed. The following species only are considered to be present in the gas: H_2, N_2, H, N, NH, NH_2, NH_3, N_2H_4. Undoubtedly, there are other species and ions present, such as N_2H_3, but the concentrations of these will be negligible compared to those considered here. It is expected that N_2H_4 will also be negligible, but we include this species because of its practical interest.

Eight equations are required in order to determine the concentrations of the eight components. Five equations express the equilibrium constants for the formation of H, N_2, NH, NH_2, and NH_3, where the data are taken from the JANAF Thermochemical Tables.[2] The sixth equation, the equilibrium constant for formation of N_2H_4, is calculated herein. The seventh equation expresses the total pressure as the sum of the partial pressures, $\Sigma_i P_i = P$. The eighth equation expresses the material balance; i.e., for the system $2N_2 + H_2$

$$2\,P_{H_2} + P_H + 0.5\,P_{NH} + 1.5\,P_{NH_2} + 2.5\,P_{NH_3} + 3\,P_{N_2H_4} - P_{N_2} - 0.5\,P_N = 0,$$

and for the system $N_2 + 8H_2$

$$8\,P_N + 16\,P_{N_2} + 7\,P_{NH} + 6\,P_{NH_2} + 5\,P_{NH_3} + 12\,P_{N_2H_4} - P_H - 2\,P_{H_2} = 0.$$

The set of eight equations were solved for the different temperatures and pressures of one and a thousand atmospheres on a computer. A single pass in the computation was sufficient. Figures 1 to 4 summarize the results.

The partial pressure of N_2H_4, as suspected, is negligible in all of the systems, although it goes through a maximum. The partial pressure of NH_3 decreases rapidly with increasing temperature, showing the low stability of this species at the high temperatures. It is interesting to note the stability of N_2 even at 5000°C, as evidenced by the small decrease in partial pressure of this species from 1000° to 5000°K.

There is only a very small effect on the concentration of the species NH, NH_2, N_2H_4, and NH_3 by varying the ratio of N_2:H_2. However, an increase in pressure from one to 1000 atmospheres does cause a slight shift in equilibrium, so that the relative concentrations of NH_3, N_2H_4, and NH_2 increases slightly.

Thermodynamic Properties of N_2H_4

Scott, et al,[3] have reported thermodynamic propertiesof N_2H_4 to 1500°K. We extend these data to 5000°K by using the more recent spectroscopic data of Giguere and Liu.[4] The latter workers were unable to determine the symmetrical stretching (ν_2) and torsional (ν_7) vibrations, so that we use the values of Scott, et al, for these two frequencies. The three components of the moment of inertia, the potential barrier to internal rotation, the reduced moment calculated by Pitzer's formula,[5] and the heat of formation at absolute zero are those given by Scott. Table I summarizes the spectroscopic data.

In the calculation of the equilibrium constants of N_2H_4, the free energy functions of H_2 and N_2 were obtained from the tables of the U.S. Bureau of Standards.[6] Table II summarizes the thermodynamic data.

The values of the thermodynamic functions calculated by us differ from those of Scott[3] by 1.5 to 3.5% in the different functions in the range 1000° to 1500°K, since the vibrational contributions in this work are based on the more recent data of Giguere and Liu.[4] The free energy of formation and - log K_p for this temperature region are about 1.5% and 2% higher, respectively, than those of Scott and co-workers.

Acknowledgement

We thank Miss Rosella Freedman for the computer calculations.

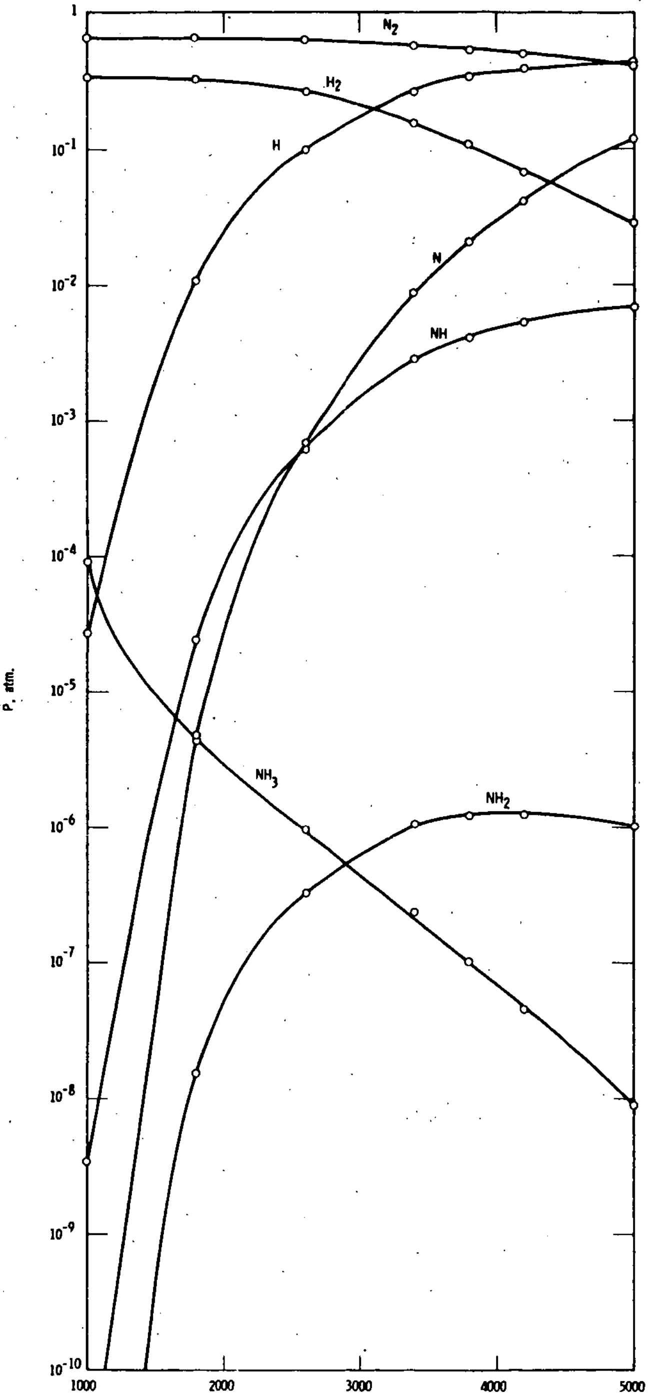

Fig. 1—Partial pressure as function of temperature for system $2N_2 + H_2$ at total pressure of 1 atmosphere.

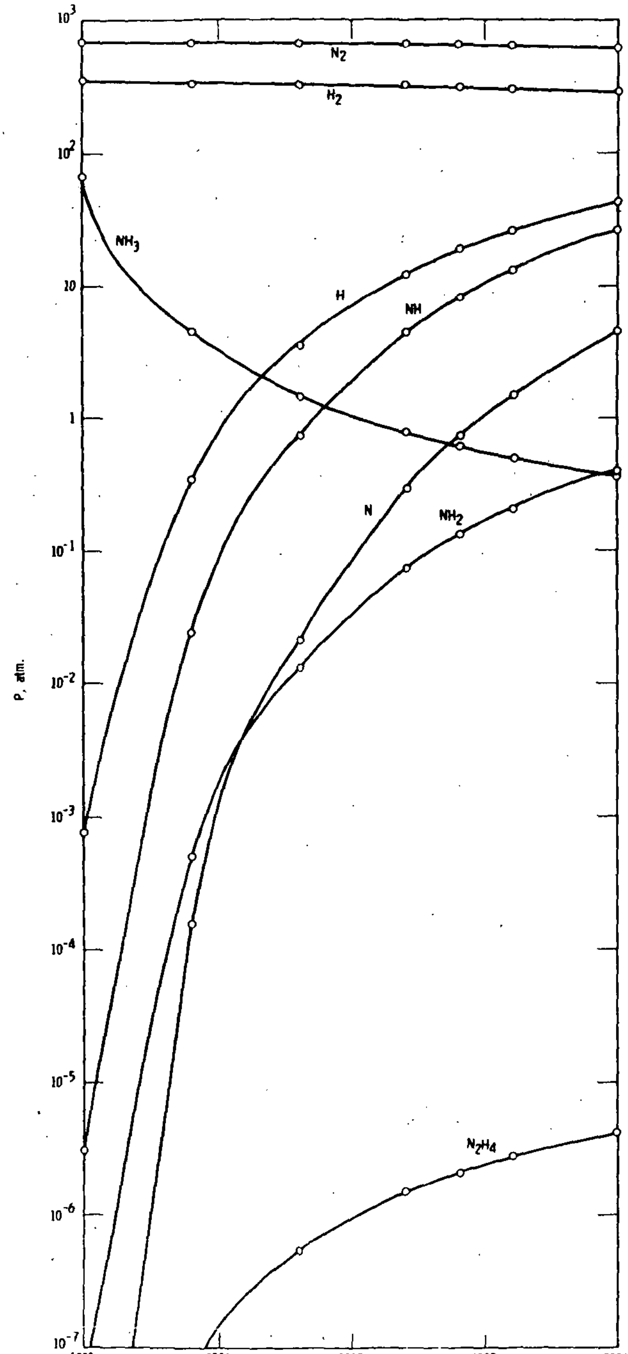

Fig. 2—Partial pressure as function of temperature for system $2N_2 + H_2$ at total pressure of 1000 atmospheres.

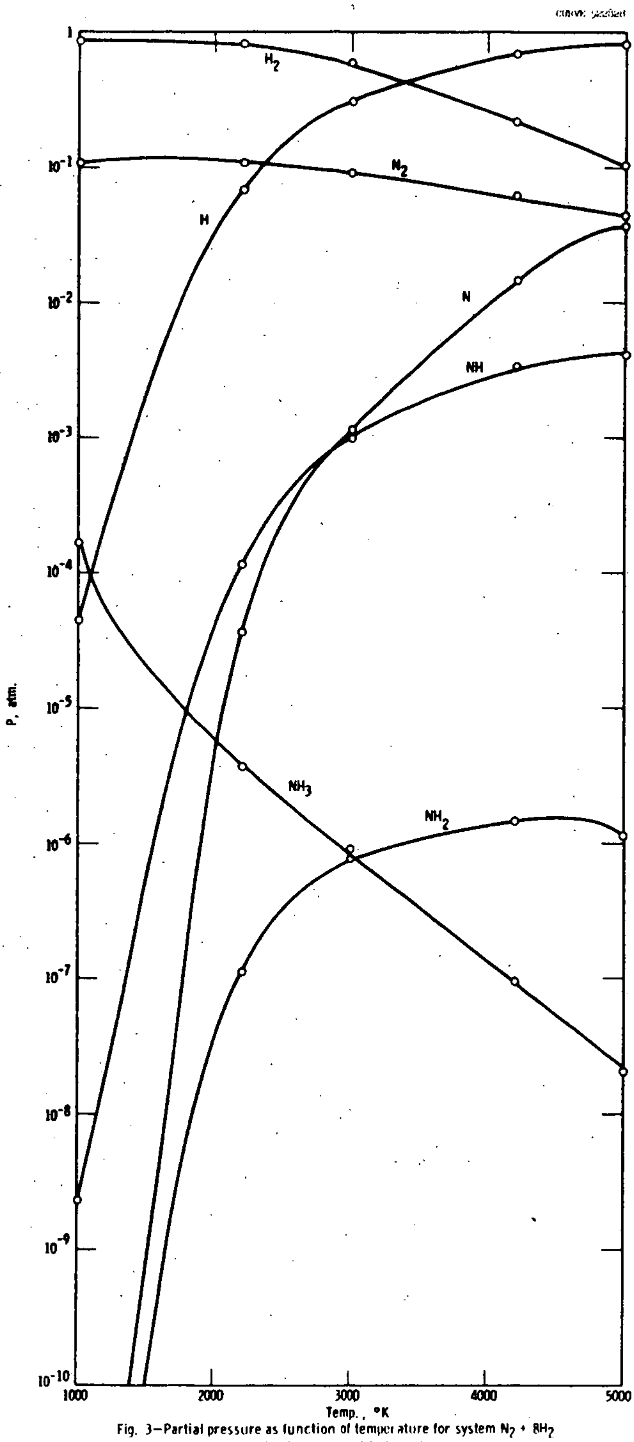

Fig. 3—Partial pressure as function of temperature for system $N_2 + 8H_2$ at total pressure of 1 atmosphere.

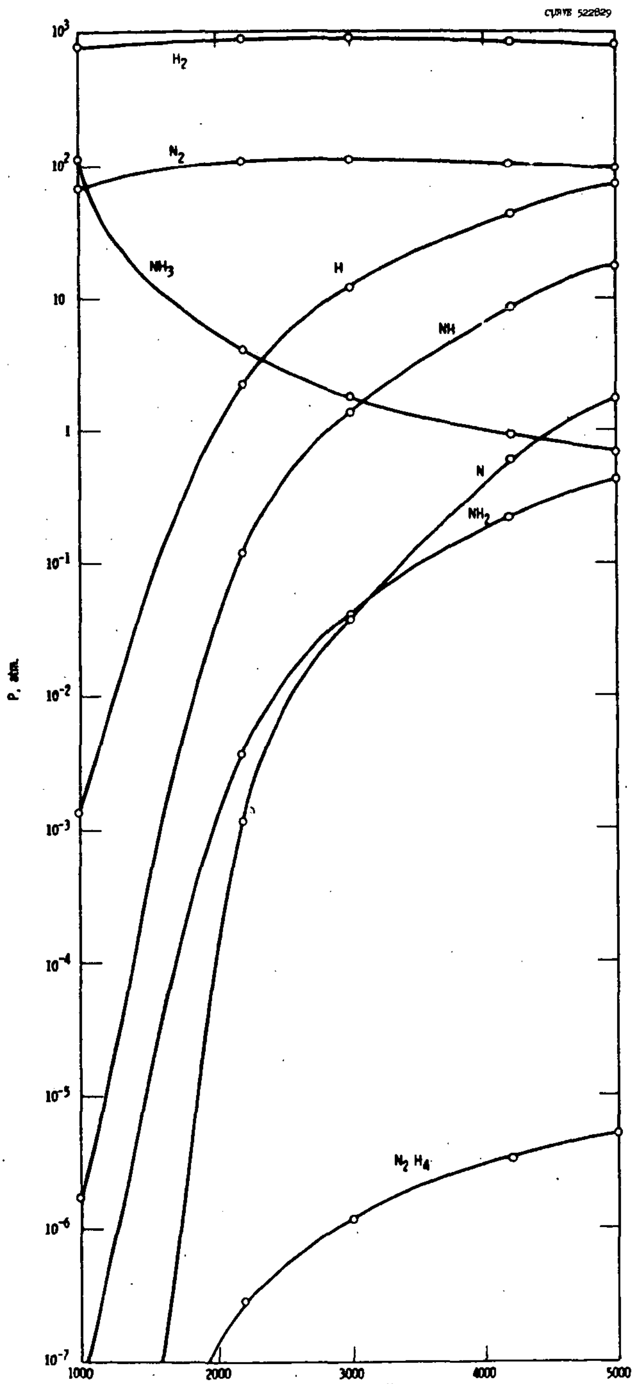

Fig. 4—Partial pressure as function of temperature for system $N_2 + 8\ H_2$ at total pressure of 1000 atmospheres.

TABLE I

MOLECULAR DATA FOR HYDRAZINE

Vibrational Frequency

Mode	cm^{-1}	Mode	cm^{-1}
ν_1	3325	ν_8	3350
ν_2	3160	ν_9 (doublet)	3280 3314
ν_3	1493	ν_{10}	1628
ν_4	1098	ν_{11}	1275
ν_5	960	ν_{12} (doublet)	933 966
ν_6	780		
ν_7	360		

Symmetry number (σ) = 2

Molecular Weight = 32.048

Moments of Inertia

$I_A = 6.18 \times 10^{-40}$ g cm^2

$I_B = 35.33 \times 10^{-40}$ g cm^2

$I_C = 36.98 \times 10^{-40}$ g cm^2

Reduced moment for internal rotation = 1.53×10^{-40} g cm^2

Potential barrier height for internal rotation = 2800 cal/mole

ΔH_o^o = 26,060 cal/mole

Statistical weight of electronic ground state = 1

TABLE II

THERMODYNAMIC FUNCTIONS, FREE ENERGY OF FORMATION AND EQUILIBRIUM CONSTANT OF N_2H_4 FROM 1000° TO 5000°K

Temp. °K	Cp, Cal/Mole	$\frac{H^\circ - H^\circ_0}{T}$ k Cal/Mole Deg.	S°, Cal/Mole/Deg.	$\frac{F^\circ - H^\circ_0}{T}$ k Cal/Mole Deg.	F°_f, k Cal/Mole	$-\log K_p$
1000	21.95	15.21	76.06	61.64	77.18	16.89
1800	26.60	19.39	90.40	71.65	122.88	14.94
2600	28.50	21.92	100.54	79.24	167.83	14.12
3400	29.38	23.60	108.30	85.37	212.09	13.65
3800	29.64	24.21	111.58	88.01	234.14	13.48
4200	29.84	24.75	114.54	90.46	256.04	13.34
5000	30.12	25.57	[illegible]	94.36	299.54	13.11

REFERENCES

1. Kroepelin, H., Kipping, D.E., and Pietruck, H., "Progress in International Research on Thermodynamic and Transport Properties," Ed. J. F. Masi and D. H. Tsai, pp. 626-648, American Society of Mechanical Engineers, Academic Press, New York, 1962.

2. "JANAF Thermochemical Tables," Vol. II, 1960.

3. Scott, D. W., Oliver, G. D., Gross, M. E., Hubbord, W. N., Huffman, H. M., J. Am. Chem. Soc., 71 2293 (1949).

4. Giguere, P. A., and Liu, I. D., J. Chem. Phys., 20, 136 (1952).

5. Pitzer, K. S., and Gwinn, W. D., J. Chem. Phys., 10, 428 (1942).

6. U. S. Bureau of Standards Circ. 564, 1955.