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PHYSICAL & THERMODYNAMIC PROPERTIES 6

Ammonia and Hydrazine

Here are experimental and calculated physical and thermodynamic data for ammonia and hydrazine—for both the liquid and gas states—over a wide range of temperatures.

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Ammonia—one of the largest-volume inorganic chemicals in the chemical process industries—has major applications in the production of fertilizers, nitrates, sulfates, phosphates, explosives, plastics, resins, amines, amides, textiles, etc. Closely related to ammonia is hydrazine, important as a component of rocket propellants.

Critical Properties—Table 6—1

Experimental critical-constant data are available for ammonia [*2,6,9,10,12,13,14,93*]. For hydrazine, experimental critical-temperature and pressure data have been reported [*2,14,189*]. The critical volume for hydrazine was estimated by means of the Herzog method [*198*]. This method provided good results for ammonia, with deviations of only 2.2%.

Heat of Vaporization—Fig. 6—1

Data at the normal boiling point were extended by means of the Watson correlation—Eq. (1—1), June 10, p. 71. Correlation values agreed closely with experimental data: less than 1% deviation for ammonia, 5% for hydrazine (with only four data points).

Vapor Pressure—Fig. 6—2

Vapor-pressure data for both ammonia and hydrazine cover the complete liquid state. In most cases, deviations are less than 1% for ammonia, and 2.5% for hydrazine (below its boiling point).

Heat Capacity—Fig. 6—3 and 6—4

Heat-capacity data (from various sources) for an ideal gas are generally in close agreement. In most instances, average deviations are less than 4% for both ammonia and hydrazine.

Liquid heat-capacity data for ammonia are available from the melting point to near the critical temperature. For hydrazine, data were extended by means of the density-extrapolation relationship—Eq. (1—3), with $n = \frac{1}{4}$—up to 190°C. The Watson method [*14*] was used for higher temperatures. These two correlations matched experimental data best, with deviations for ammonia being less than 1%.

Density—Fig. 6—5

Data for ammonia were expanded to cover the full liquid state using pressure-volume-temperature (PVT) relationships [*200,209*], with maximum deviations between experimental and calculated values of 1%. Data for hydrazine were extended using Lu's correlation—Eq. (2—2), July 8, p. 85. Application of this correlation to

(*Text continues on p. 99*)

About the Series

This ammonia-hydrazine section—the sixth part of this year's series on the physical and thermodynamic properties of chemicals—has been preceded by:

Part 1 (June 10): The Halogens (Cl_2, Br_2, F_2, I_2)
Part 2 (July 8): Sulfur Oxides (SO_2, SO_3)
Part 3 (Aug. 19): Nitrogen Oxides (N_2O, NO, NO_2)
Part 4 (Sept. 30): Carbon Oxides (CO, CO_2)
Part 5 (Oct. 28): Halogen Acids (HCl, HF, HBr, HI)

Still to be published are six more parts that will cover: diatomic gases (H_2, O_2, N_2), inert gases, major non-halogen acids, prominent ammonia derivatives, hydrogen oxides, others.

How To Use the Graphs

Each graph is outfitted with a key that lists references and explains just what part of the curve is determined experimentally, and what part is estimated from theoretical correlations.

The shaded squares denote the following:

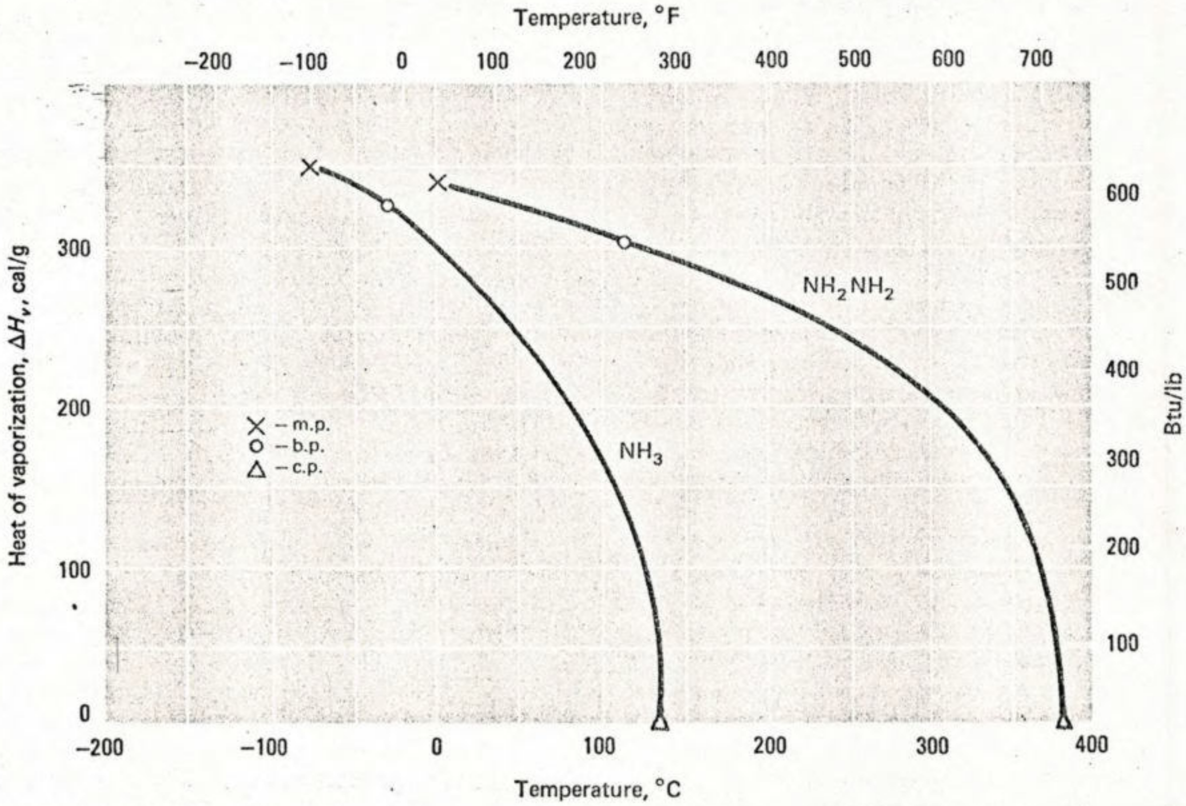
- ■ Data in this region are experimentally known.
- ◪ Experimental and correlated data used.
- □ All data in this region are correlated.

The "regions" referred to are the temperature ranges between the melting, boiling and critical points (m.p., b.p. and c.p., respectively), or in some cases, the specific temperatures noted in the key.

Physical Properties of Anhydrous Ammonia and Hydrazine—Table 6–1

Identification	Ammonia, NH_3	Hydrazine, NH_2NH_2
State (std. conditions)	Gas	Liquid
Molecular weight, M	17.032	32.048
Boiling point, T_b, °C	−33.43	113.5
Melting point, T_m, °C	−77.74	2.0
Critical temp., T_c, °C	132.4	380
Critical pressure, P_c, atm	111.3	145
Critical volume, V_c, cm^3/g-mol	72.4	101.1*
Critical compressibility factor, Z_c	0.243	0.275*

*Estimated



Heat of Vaporization — Fig. 6–1

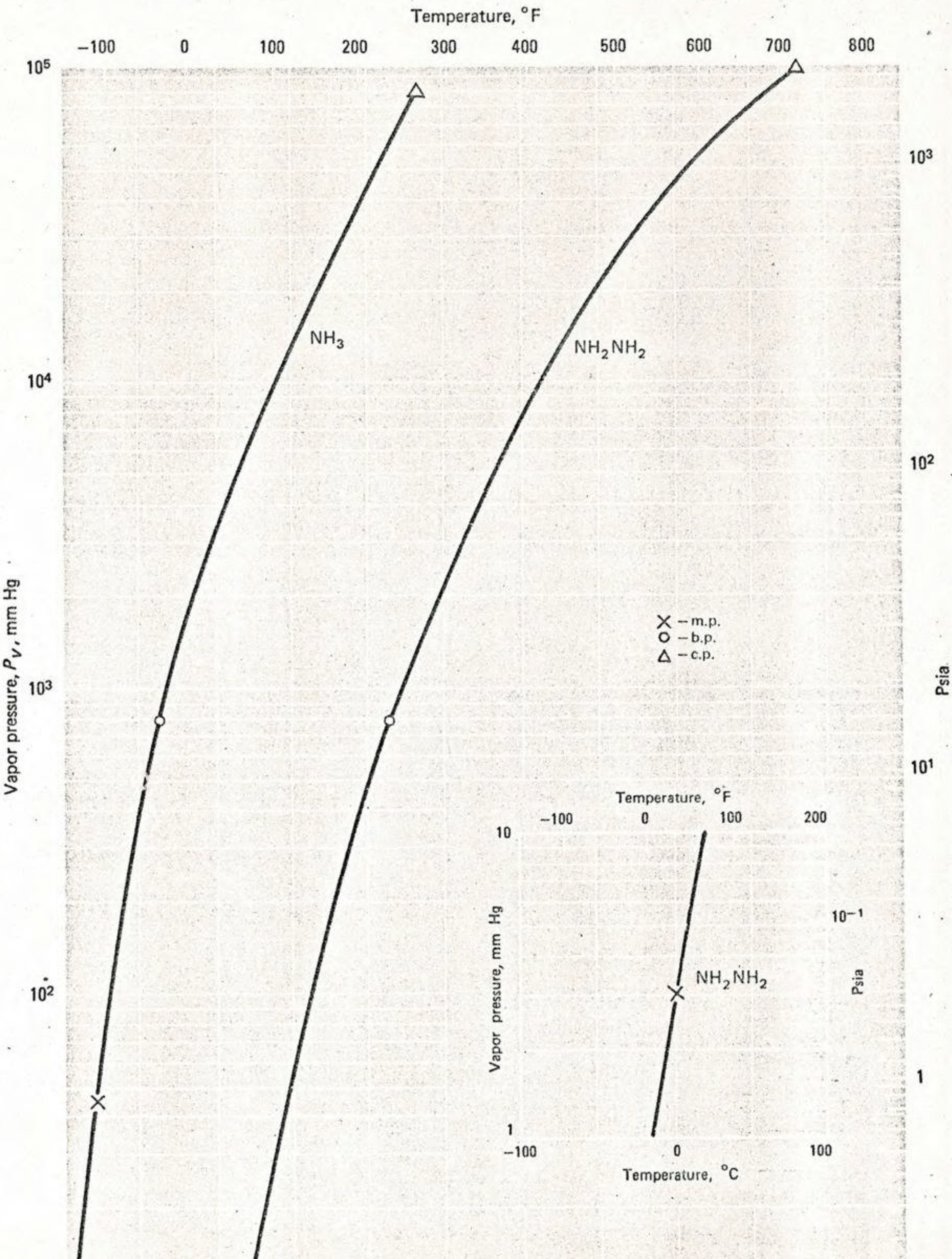
Fig. 6–1	Temperature Range m.p.–b.p.	Temperature Range b.p.–c.p.	References
Ammonia	■	■	2, 6, 9, 10, 13, 14, 194
Hydrazine	◪	□	14, 189, 195, 206, 218

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

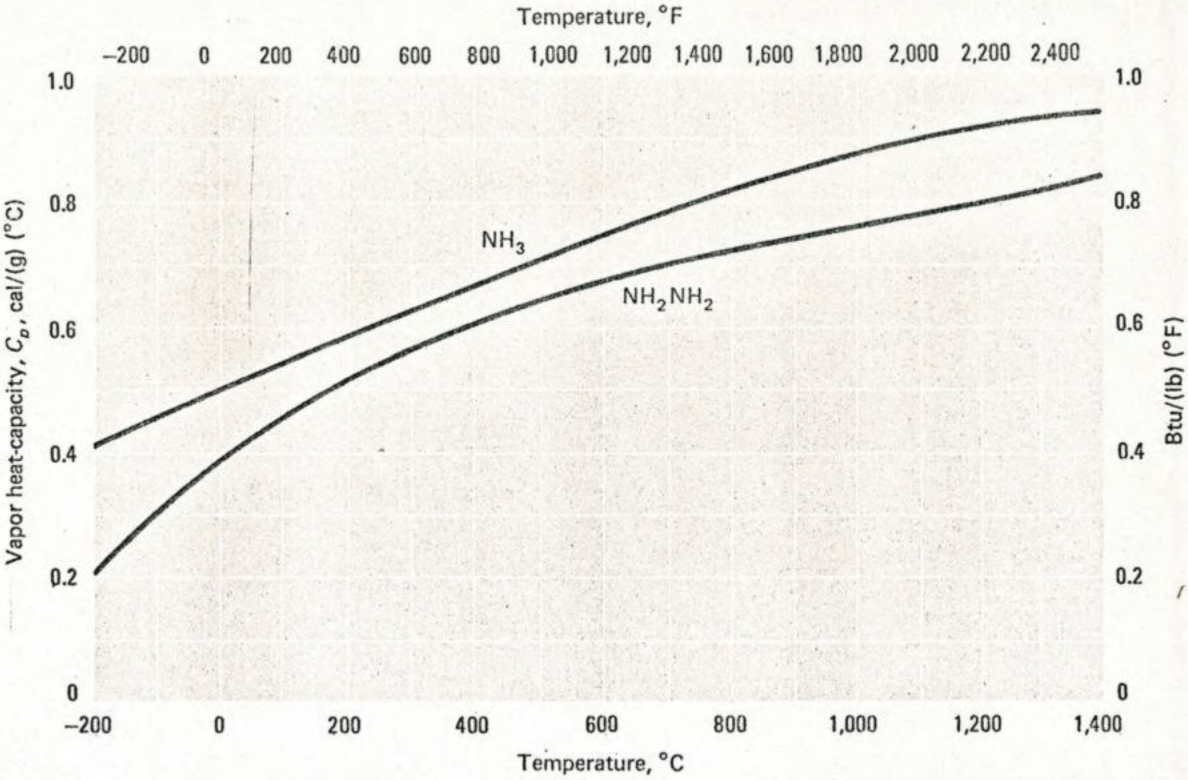
Fig. 6–2	Temperature Range m.p.–b.p.	Temperature Range b.p.–c.p.	References
Ammonia	■	■	2, 6, 9, 10, 13, 17, 194
Hydrazine	■	■	189

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Vapor Pressure — Fig. 6–2 →



Temperature, °F
-100
0
100
200
300
400
500
600
700
800
10⁵
10⁴
10³
10²
10¹
Vapor pressure, P_V, mm Hg
NH₃
NH₂NH₂
× – m.p.
o – b.p.
Δ – c.p.
10³
10²
10¹
1
Psia
-100
0
100
200
300
400
Temperature, °C
Temperature, °F
-100
0
100
200
10
1
Vapor pressure, mm Hg
NH₂NH₂
10⁻¹
Psia
-100
0
100
Temperature, °C



Vapor Heat Capacity – Fig. 6–3

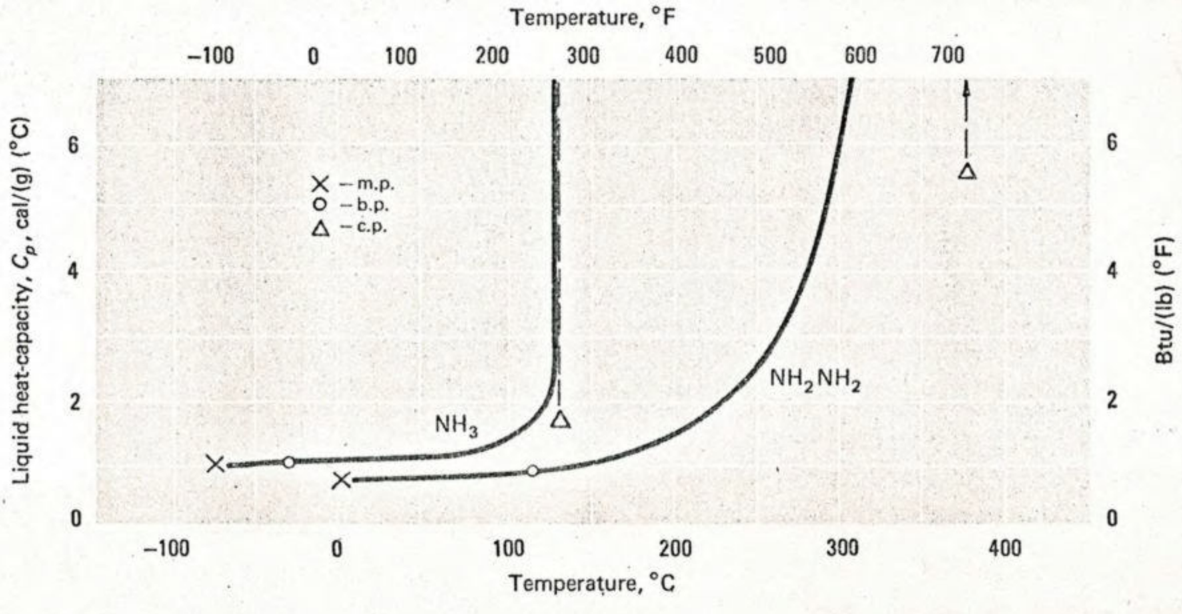
Fig. 6–3	Temperature Range, °C			References
	0–500	500–1,000	1,000–1,500	
Ammonia	◪	◪	◪	2,6,7,9,12,13,14,15,18,19,20,194,203
Hydrazine	◪	◪	◪	7,14,15,189,218

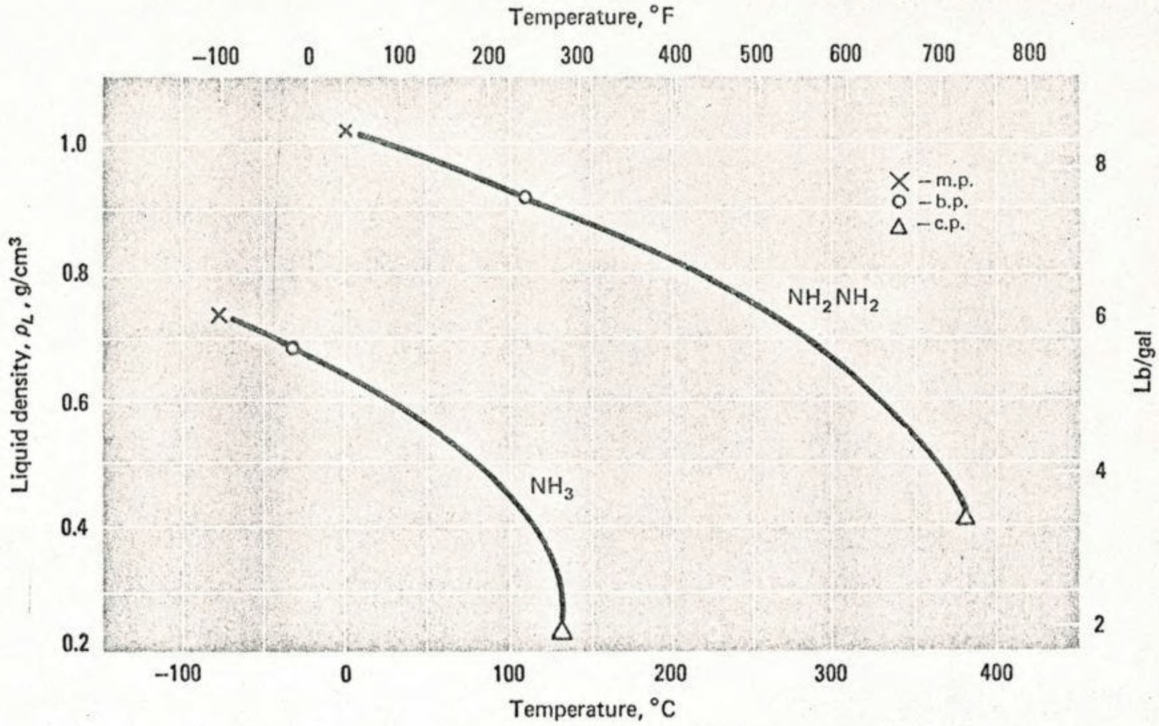
■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Fig. 6–4	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Ammonia	■	■	6,12,13,19,194
Hydrazine	◪	□	6,14,20,215,218

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Liquid Heat Capacity – Fig. 6–4





Liquid Density – Fig. 6–5

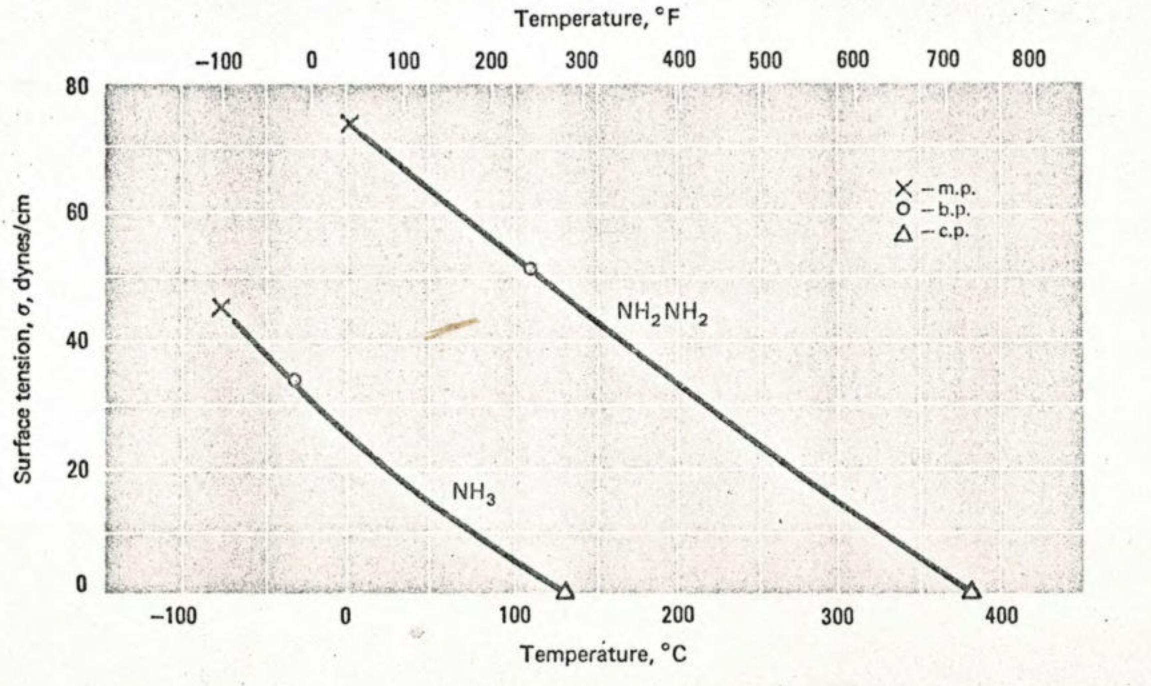
Fig. 6–5	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Ammonia	◩	■	2,4,6,12,14,194,200,205,209
Hydrazine	◩	□	4,14,189

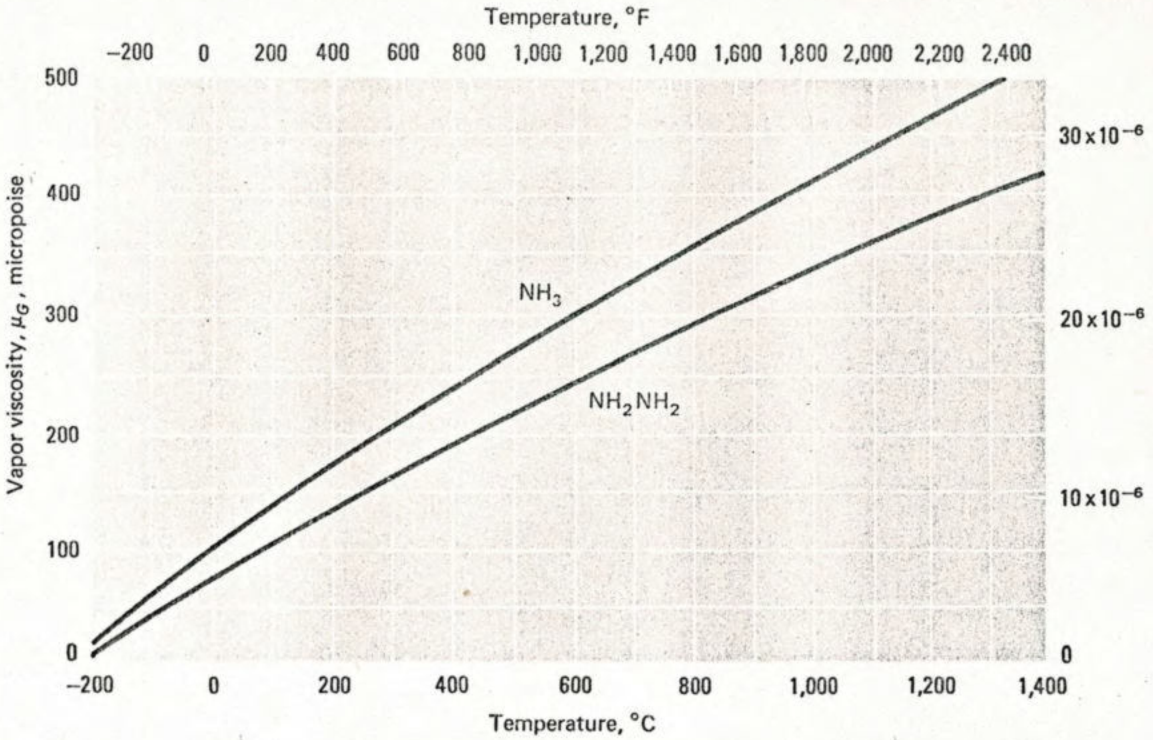
■ Laboratory data ◩ Laboratory plus correlations □ All correlated data

Fig. 6–6	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Ammonia	◩	◩	2,6,12,53,79
Hydrazine	◩	□	4,53,189,190,214

■ Laboratory data ◩ Laboratory plus correlations □ All correlated data

Surface Tension – Fig. 6–6





Vapor Viscosity – Fig. 6–7

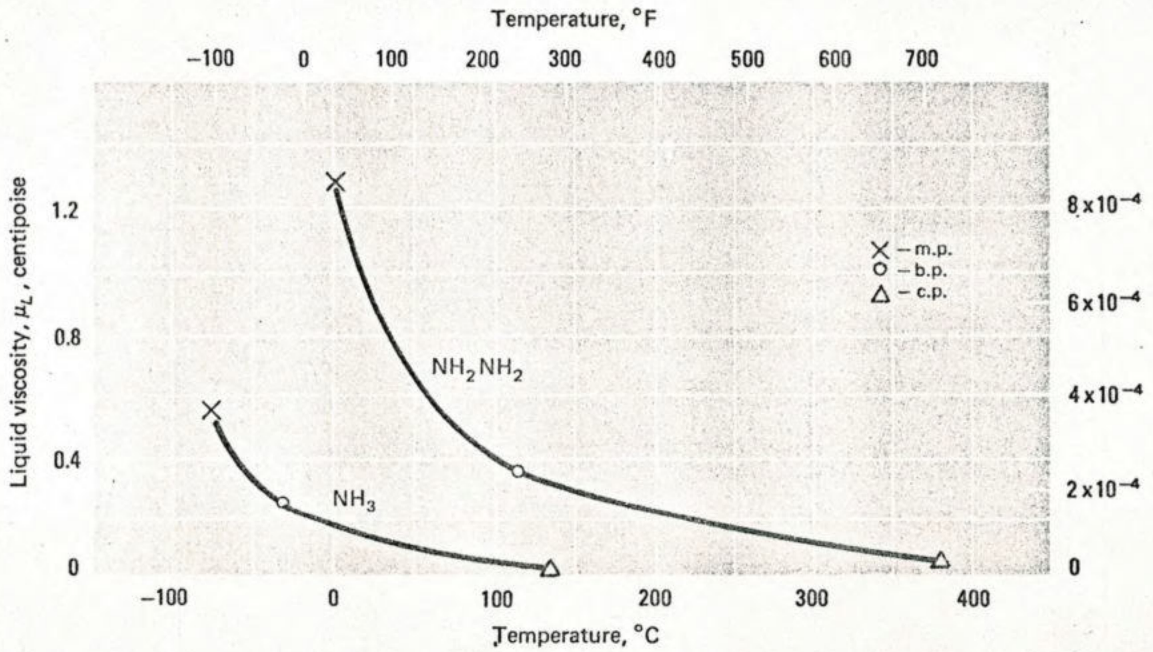
Fig. 6–7	Temperature Range, C			References
	0–500	500–1,000	1,000–1,500	
Ammonia	◩	■	◩	2, 12, 14, 89, 173, 192, 207, 223, 224, 225, 226, 227
Hydrazine	□	□	□	14, 173, 225, 226, 227

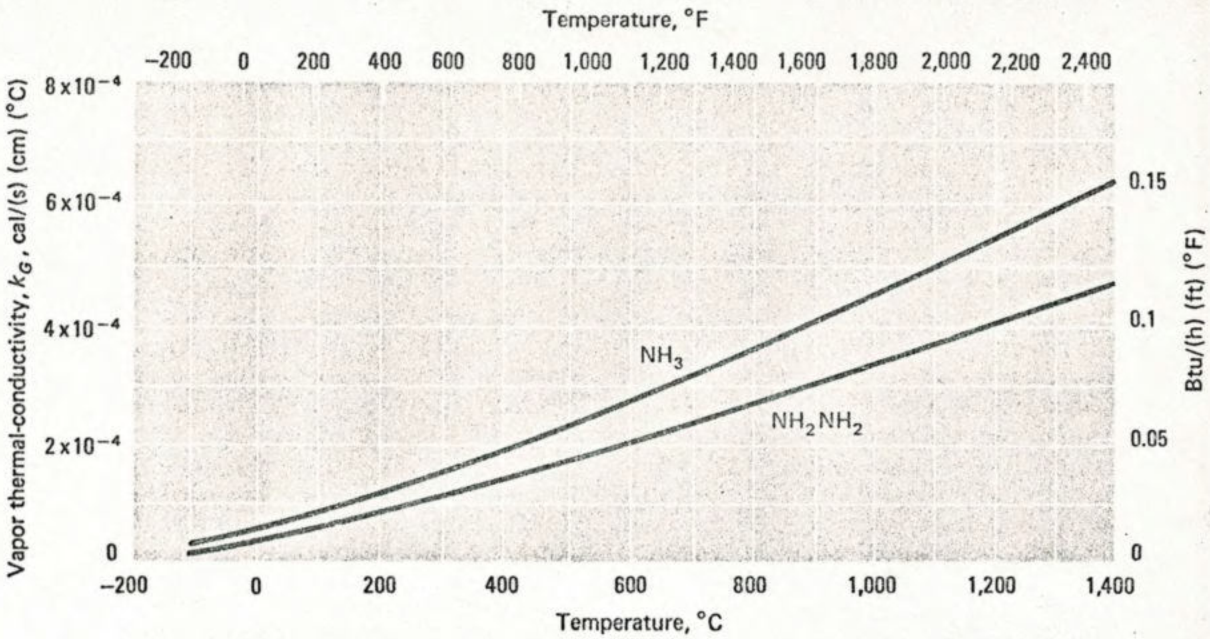
■ Laboratory data ◩ Laboratory plus correlations □ All correlated data

Fig. 6–8	Temperature Range		Referances
	m.p.–b.p.	b.p.–c.p.	
Ammonia	◩	◩	2, 12, 14, 188, 192, 207, 213, 222, 224
Hydrazine	◩	□	4, 14, 173, 189, 208, 233

■ Laboratory data ◩ Laboratory plus correlations □ All correlated data

Liquid Viscosity – Fig. 6–8





Vapor Thermal Conductivity – Fig. 6–9

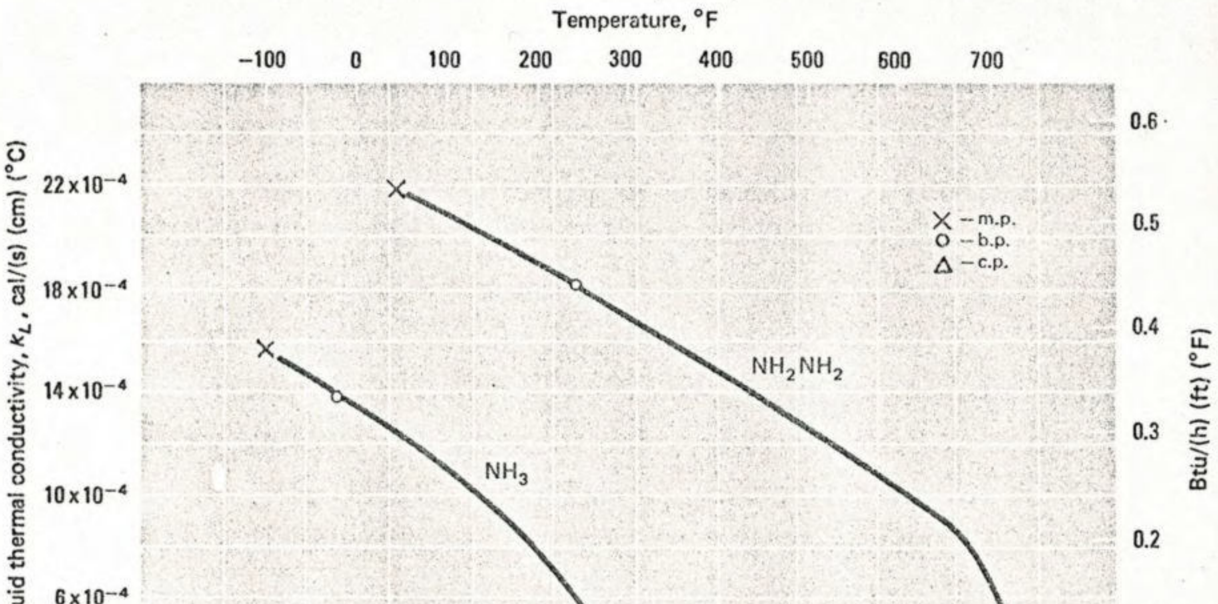
Fig. 6–9	Temperature Range, °C			References
	0–500	500–1,000	1,000–1,500	
Ammonia	■	◩	□	12, 13, 14, 18, 19, 207
Hydrazine	□	□	□	13, 14

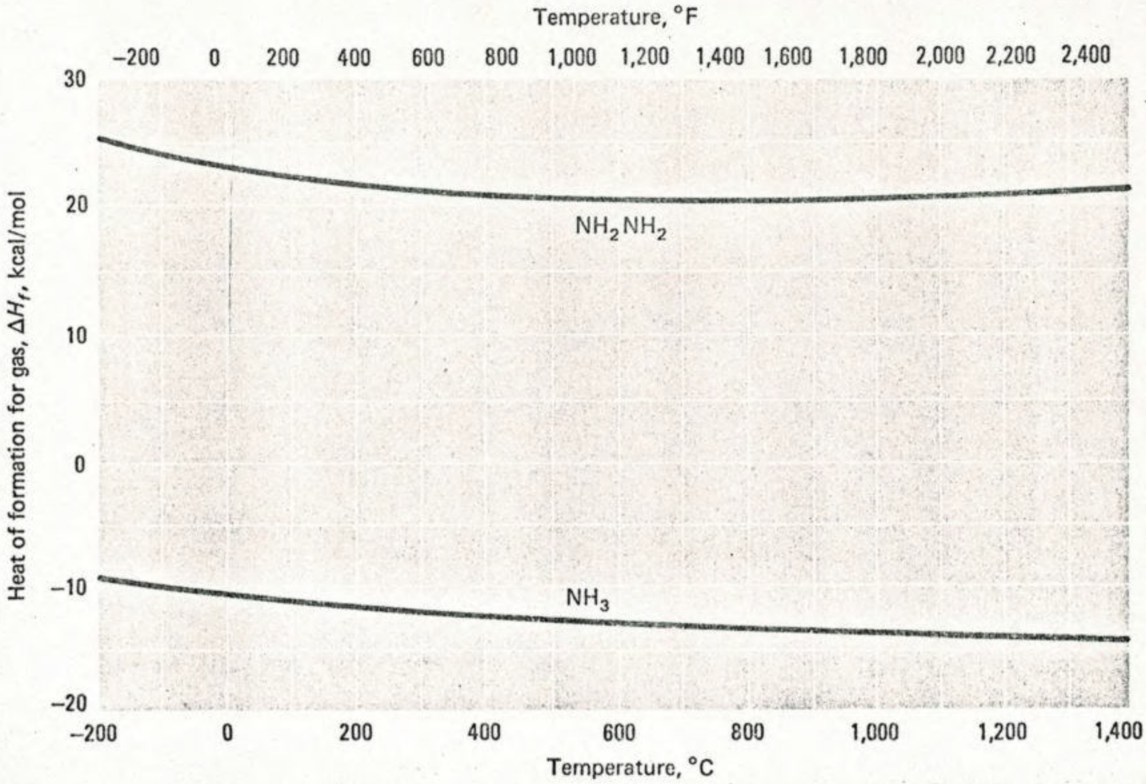
■ Laboratory data ◩ Laboratory plus correlations □ All correlated data

Fig. 6–10	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Ammonia	◩	◩	13, 14, 19, 207
Hydrazine	□	□	13, 14

■ Laboratory data ◩ Laboratory plus correlations □ All correlated data

Liquid Thermal Conductivity – Fig. 6–10





Heat of Formation for Gas – Fig. 6–11

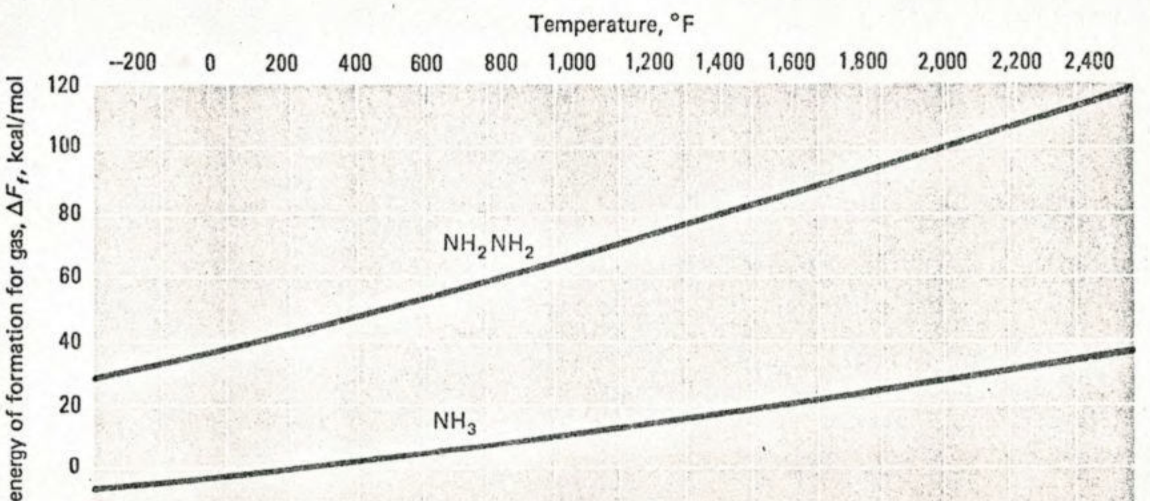
Fig. 6–11	Temperature Range, °C			References
	0–500	500–1,000	1,000–1,500	
Ammonia	◪	◪	◪	7,12,15,20,21,197,203
Hydrazine	◪	◪	◪	7,15,20,189,218

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Fig. 6–12	Temperature Range, °C			References
	0–500	500–1,000	1,000–1,500	
Ammonia	◪	◪	◪	7,12,15,20,21,197
Hydrazine	◪	◪	◪	7,15,20,189,197,218

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Free Energy of Formation for Gas – Fig. 6–12



ammonia gave good agreement with PVT-data results. Deviations were less than 1%.

Surface Tension—Fig. 6—6

Surface-tension data were extended using the Othmer relationship—Eq. (1—4), June 10, p. 71. Deviations were less than 0.3% for both ammonia (11 data points) and hydrazine (5 data points).

Viscosity—Fig. 6—7 and 6—8

The Svehla estimation method—Eq. (4—1), Sept. 30, p. 122—was used to extend gas-phase viscosity data for ammonia. The corresponding-states method of Stiel and Thodos [*14,173*], which follows, also gave results that agreed with available data:

$$\mu_G = \frac{1}{\xi} f(T_r, Z_c) \qquad (6\text{—}1)$$

where μ_G is viscosity, centipoise; $\xi = T_c^{1/6}/(M^{1/2}P_c^{2/3})$; T_c = critical temperature, °K; P_c = critical pressure, atmospheres (atm); M = molecular weight; and reduced temperature, $T_r = T/T_c$. The term $f(T_r, Z_c)$ is available in Reid and Sherwood [*14*] or Ref. 173. For the Stiel and Thodos method, maximum deviations from actual data were less than 4.8% in the 0-300°C range. At higher temperatures, the results varied more from the Svehla estimates.

Gas-phase viscosity for hydrazine was estimated by means of the Stiel and Thodos method, which was given the same adjustment required to bring the results in agreement with Svehla estimates at higher ammonia temperatures. The results for hydrazine are assumed to represent correct order-of-magnitude values.

Liquid-viscosity data for ammonia were extended using the Stiel and Thodos method [*14*]:

$$\mu_L = \frac{1}{\xi} g(T_r, Z_c) \qquad (6\text{—}2)$$

where μ_L is viscosity, centipoise; and $\xi = T_c^{1/6}/(M^{1/2}P_c^{2/3})$. The term $g(T_r, Z_c)$ is available from the generalized plot in Reid and Sherwood [*14*]. This method gave results that agreed with experimental data; deviations were less than 1%.

Liquid-viscosity data for hydrazine were extended by means of the Guzman-Andrade relationship—Eq. (1—6), June 10, p. 71—in the melting-to-boiling-point interval, and the Stiel and Thodos method in the boiling-to-critical-point interval. Comparison of correlation results with available data showed deviations of less than 1.2%.

Thermal Conductivity—Fig. 6—9 and 6—10

Gas thermal-conductivity data for ammonia have been analyzed by Touloukian et al. [*19*], who have also presented tabulated results for the best data fit. Bromley's correlation [*13,14*] was used to extend the data to higher temperatures:

$$k_G = \frac{\mu_G}{M} f(C, T_r, \alpha) \qquad (6\text{—}3a)$$

where k_G = gas thermal conductivity, cal/(cm)(s)(°C); μ_G = viscosity, poise; M = molecular weight, g/(g-mol); C = heat-capacity contributions; and T_r = reduced temperature, T/T_c. The term α, which represents boiling-point properties, is defined as:

$$\alpha = \frac{3.0\rho_{lb}}{M}\left(\frac{\Delta H_{vb}}{T_b} - 8.75 - R \ln T_b\right) \qquad (6\text{—}3b)$$

where ρ_{lb} = density of liquid at boiling point, g/cm^3; ΔH_{vb} = heat of vaporization at boiling point, cal/(g-mol); T_b = boiling point, °K; and R = gas constant = 1.987 cal/(g-mol)(°K). The term $f(C, T_r, \alpha)$ is available from Perry's Chemical Engineers' handbook [*13*] or Reid and Sherwood [*14*].

Gas thermal conductivities for hydrazine were estimated using Bromley's correlation, with negligible internal rotational contribution. Correlation results compared favorably with available data for ammonia (more than 50 data points). Average deviations from the best data fit were less than 4.1%.

Limited liquid-thermal-conductivity (k_c) data, available only for ammonia [*19*], were extended by modification of the Schaeffer and Thodos correlation for diatomic gases:

$$k_L = k_c q(T_r, P_r) \qquad (6\text{—}4)$$

where k_c = critical thermal conductivity, cal/(cm)(s)(°C); T_r = reduced temperature; P_r = reduced pressure; and $q(T_r, P_r)$ = functional relationship of reduced temperature and reduced pressure, which is available from the plot in Perry's Chemical Engineers' Handbook [*13*] or Reid and Sherwood [*14*]. The major modification consisted of determining, for the liquid, the critical conductivity from experimental data (exp.) and the Schaeffer and Thodos (S&T) relationship as follows:

$$k_c = \frac{(k_L)_{\text{exp.}}}{[q(T_r, P_r)]_{\text{S\&T}}} \qquad (6\text{—}5)$$

Correlation results and experimental values were in close agreement. Deviations from the best data fit were less than 2.5% for ammonia (six data points).

Liquid thermal conductivity for hydrazine was estimated by means of the modified Schaeffer and Thodos correlation, Eq. (6—4). Here, the initial modification involved determination of the critical thermal conductivity (k_c) using the relationship for the gas:

$$k_c = \frac{(k_G)_{\text{Bromley}}}{[f(T_r, P_r)]_{\text{S\&T}}} \qquad (6\text{—}6)$$

where k_G values can be calculated from the Bromley correlation, Eq. (6—3), and $f(T_r, P_r)$ values can be obtained from the graphical plot in Perry's Handbook [*13*], or Reid and Sherwood [*14*]. The average k_c value thus determined is substituted into the Schaeffer and Thodos correlation, Eq. (6—4), for estimation of the liquid thermal conductivity.

The accuracy of the technique is not precisely known for hydrazine, because liquid data were not identified in the extensive literature search. However, application of the method to ammonia showed good order-of-magnitude agreement, with deviations from the best data fit being less than 20%.

Heat and Free Energy of Formation—Fig. 6—11, 6—12

Heat and free energy of formation results for an ideal gas—obtained from various sources—are in agreement for both ammonia and hydrazine.

Stability of Ammonia and Hydrazine

In obtaining properties of mixtures that contain ammonia and hydrazine, pure-component data are required. Property data for these pure compounds are presented over a wide temperature range, even though it would be most difficult to isolate the pure components at higher temperatures (because of their instability). This should be remembered when examining and making use of the physical and thermodynamic property data presented here.

Ammonia, which is a comparatively stable gas at ordinary temperatures, begins to decompose at about 450–500°C [*4*], with decomposition increasing at higher temperatures. Hydrazine decomposes into nitrogen and ammonia at about 350°C [*4*], and into the elements at more elevated temperatures.

The physical and thermodynamic data in this article are usable for the pure components in their stable temperature ranges, and for mixtures over the wider temperature ranges. #

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