PHYSICAL & THERMODYNAMIC PROPERTIES

Hydrogen Halides: HF, HCl, HBr, HI

Properties of these industrially vital anhydrous hydrogen halides are presented in graphs derived from experimental data and theoretical correlations.

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Hydrogen halides are important industrially:

Hydrogen fluoride for producing inorganic and organic compounds, and as a catalyst for many reactions;

Hydrogen chloride for turning out chlorinated solvents, and vinyl and alkyl chlorides;

Hydrogen bromide for making inorganic bromides, and for organic reactions, both as reagent and catalyst;

Hydrogen iodide for manufacturing hydroiodic acid, and organic and inorganic iodides.

Critical Properties—Table 5—1

Experimental critical property data for hydrogen fluoride agree substantially [*4,10,182,183*]. Deviations in critical temperature, pressure and volume are of the order ±3°C, ±3.38 atm and ±0.03 g/ml [*182,183*].

Experimental critical constants are available for hydrogen chloride [*2,4,10,14,83*], as are critical temperature and pressure for hydrogen bromide and iodide [*2,4,10,14,83*]. Critical volume for hydrogen bromide and iodide has been estimated by the method of Lydersen:

$$V_c = 40 + \Sigma\Delta_v \qquad (5\text{—}1)$$

Values for Δ_v are listed by Reid and Sherwood [*14*]. When the accuracy of this method was tested by applying it to the hydrogen chloride and fluoride, the deviation was 2.3% for the former and 16.0% for the latter.

Each compressibility factor was calculated by means of the ideal gas law relationship (Eq. **2**—1).

Heat of Vaporization—Fig. 5—1

Experimental data for heats of vaporization at temperatures about boiling points were expanded by means of Watson's correlation (Eq. **1**—1) for hydrogen chloride, bromide and iodide.

For hydrogen fluoride, ΔH_v has been determined experimentally over a wide temperature range, and from 0° to 105°C with the rearranged Clapeyron equation [*185*]:

$$\Delta H_v = H_v - H_L = T(V_v - V_L)(dp/dT) \qquad (5\text{—}2)$$

Vapor Pressure—Fig. 5—2

Data were analyzed and extended with the Cox-Antoine correlation method (Eq. **1**—2).

Heat Capacity—Fig. 5—3, 5—4

Heat capacities for the ideal gas at atmospheric pressure are primarily based on spectroscope and molecular structure data. Deviations were less than 1.3% for hydrogen fluoride, 3% for hydrogen chloride, 3.6% for hydrogen bromide and 5.6% for hydrogen iodide.

Liquid data at constant pressure were extended to the critical temperature by means of density extrapolation relationships (Eq. **1**—3, $n = 1$). Absolute deviations from experimental data were less than 2% except in the case of the fluoride, for which the maximum deviation from the best fitting of the data was 4%.

Density—Fig. 5—5

Data for hydrogen fluoride cover the complete liquid phase, with absolute deviations of less than 0.035 g/cm^3 from the best fitting.

For the other halides, densities have been experimentally determined over a wide temperature range and the full liquid phase by means of the Lu correlation (Eq. **2**—2). The results from the latter agree closely with the least squares fitting of the available experimental data. Deviations were less than 1.5% for the chloride, 3.1% for the bromide and 3.0% for the iodide.

Surface Tension—Fig. 5—6

Experimental data for each halide yielded a straight line when correlated with the Othmer relationship (Eq.

(Text continues on p. 122)

See Part 1 of this series, *Chem. Eng.*, June 10, 1974, for all equations starting with a boldfaced numeral "**1**"; Part 2 for those with "**2**"; etc. Part 2 appeared July 8; Part 3, Aug. 9; and Part 4, Sept. 30.

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:

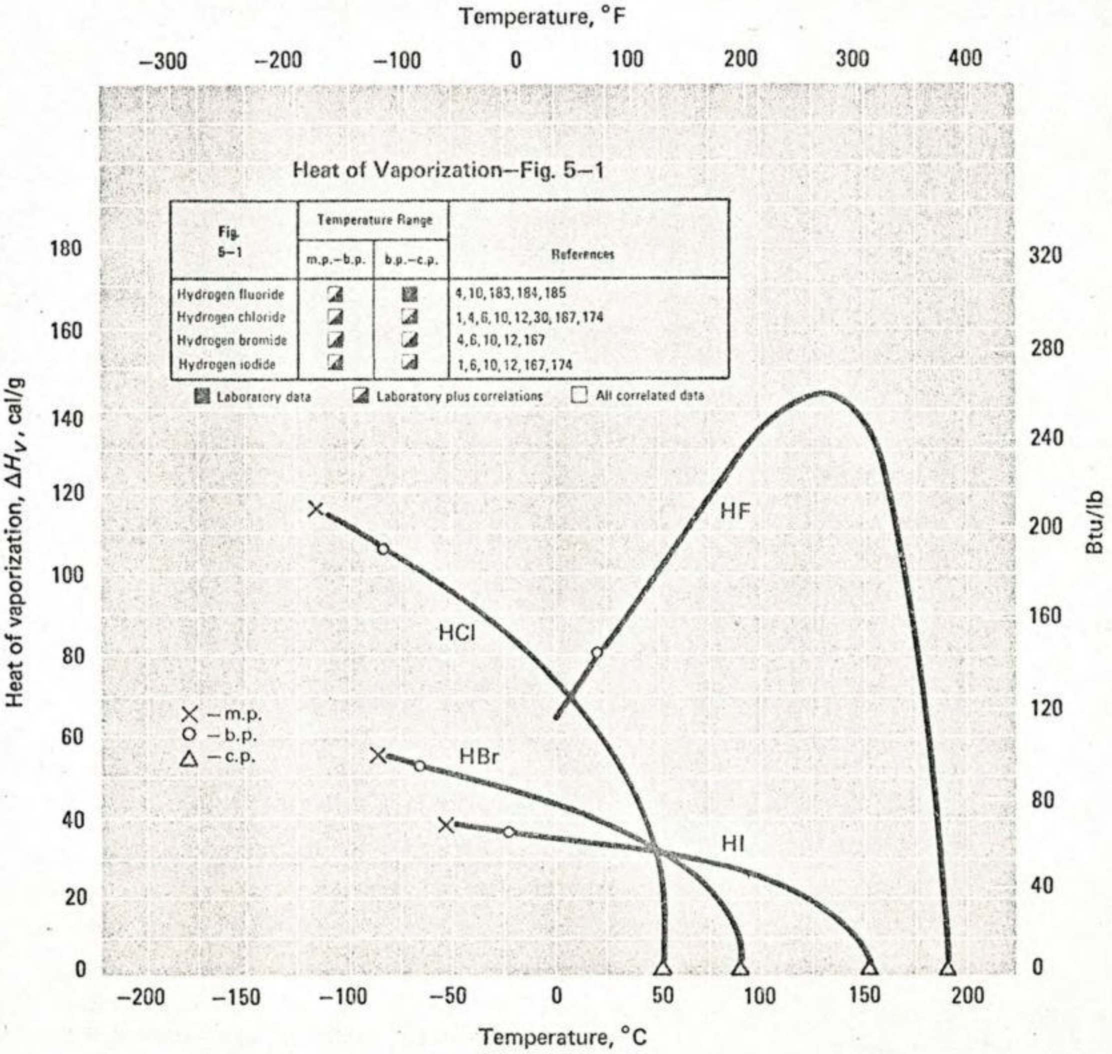
- ■ Data in this region are experimentally known.
- ◪ Experimental and correlated data used.
- ☐ All data in this region are correlated.

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 the Anhydrous Hydrogen Halides – Table 5–I

Identification	Fluorine, HF	Chlorine, HCl	Bromide, HBr	Iodide, HI
State, (std. cond.)	Gas*	Gas*	Gas*	Gas*
Molecular weight, M	20.0	36.46	80.92	127.9
Boiling point, T_b, °C	19.5	− 85.03	−66.8	−35.5
Melting point, T_m, °C	−83.5	−114.2	−86.9	−50.8
Critical temp., T_c, °C	188.0	51.5	90.0	151.0
Critical pressure, P_c, atm	64.0	82.0	84.3	82.0
Critical volume, V_c, cm^3/gr mol	69.0	87.0	110.0†	135.0†
Critical compressibility factor, Z_c	0.117	0.266	0.310†	0.318†

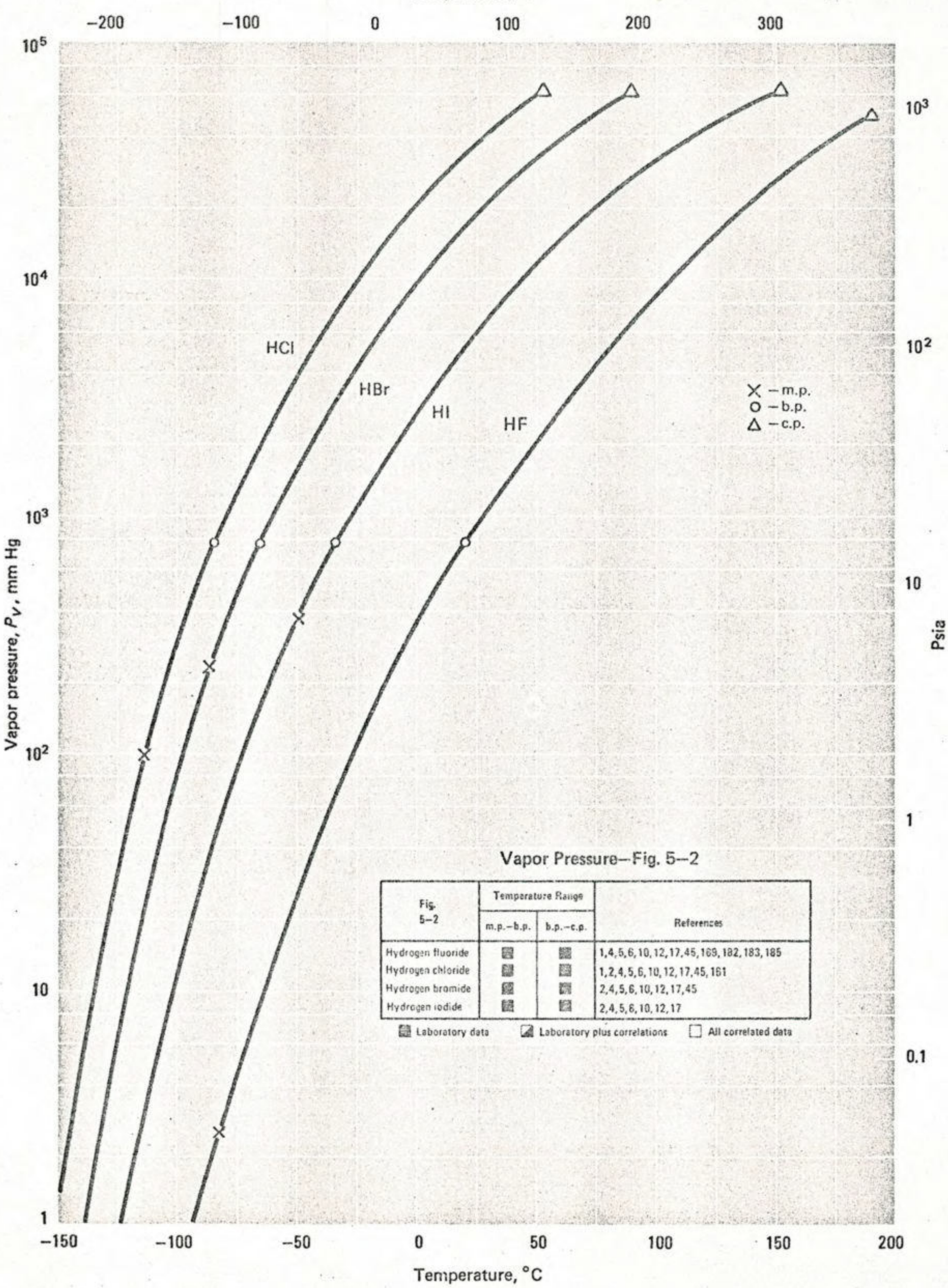
*Colorless †Estimated



Heat of Vaporization–Fig. 5–1

Fig. 5–1	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Hydrogen fluoride	◪	■	4, 10, 183, 184, 185
Hydrogen chloride	◪	◪	1, 4, 6, 10, 12, 30, 167, 174
Hydrogen bromide	◪	◪	4, 6, 10, 12, 167
Hydrogen iodide	◪	◪	1, 6, 10, 12, 167, 174

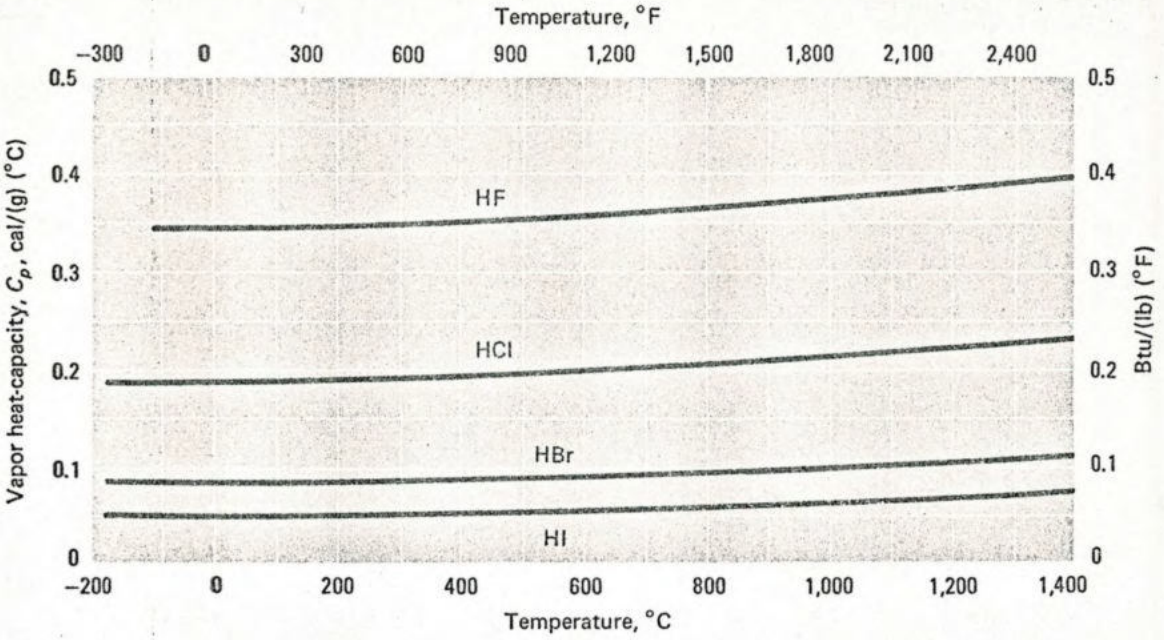
■ Laboratory data ◪ Laboratory plus correlations ☐ All correlated data



Vapor Pressure—Fig. 5–2

Fig. 5–2	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Hydrogen fluoride	▦	▦	1,4,5,6,10,12,17,45,169,182,183,185
Hydrogen chloride	▦	▦	1,2,4,5,6,10,12,17,45,161
Hydrogen bromide	▦	▦	2,4,5,6,10,12,17,45
Hydrogen iodide	▦	◩	2,4,5,6,10,12,17

▦ Laboratory data ◩ Laboratory plus correlations ☐ All correlated data



Vapor Heat Capacity—Fig. 5–3

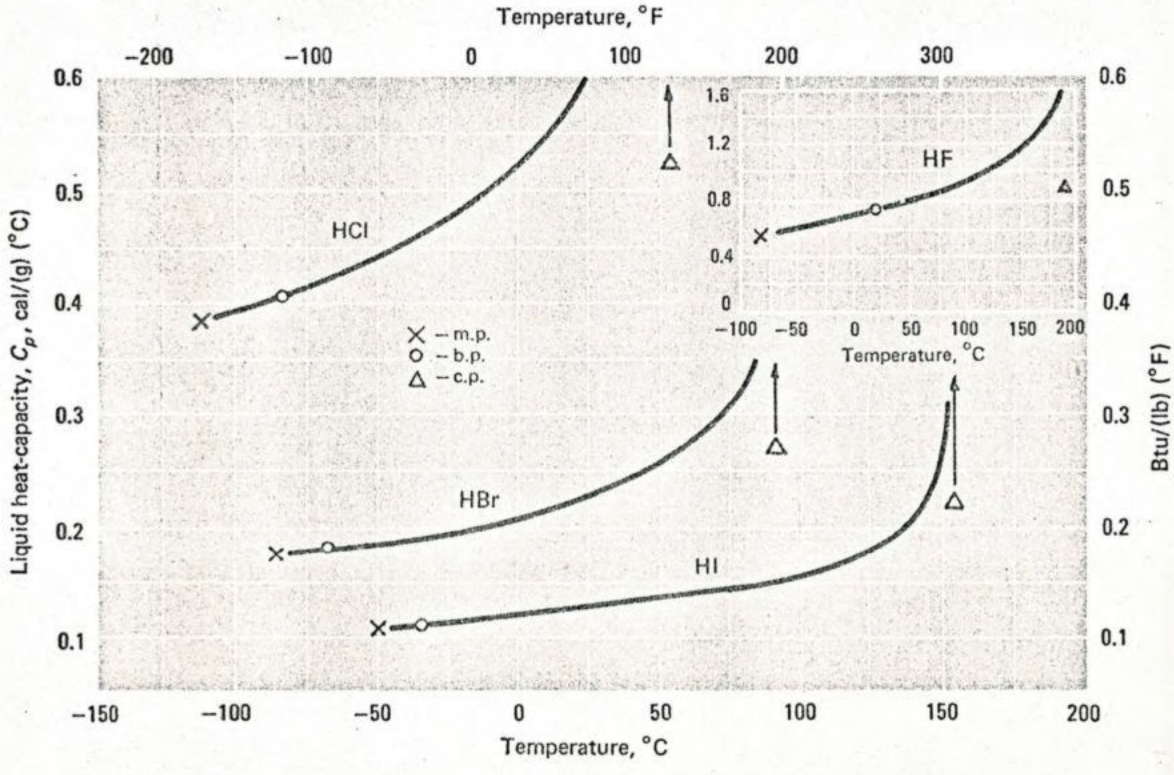
Fig. 5–3	Temperature Range, C			References
	0–500	500–1,000	1,000–1,500	
Hydrogen fluoride	◪	◪	◪	7,8,11,15,18,21,34
Hydrogen chloride	◪	◪	◪	8,10,11,12,14,15,18,19,20,21,34
Hydrogen bromide	◪	◪	◪	7,8,10,12,15,18,20,21,34
Hydrogen iodide	◪	◪	◪	7,8,10,12,15,18,19,20,21,34

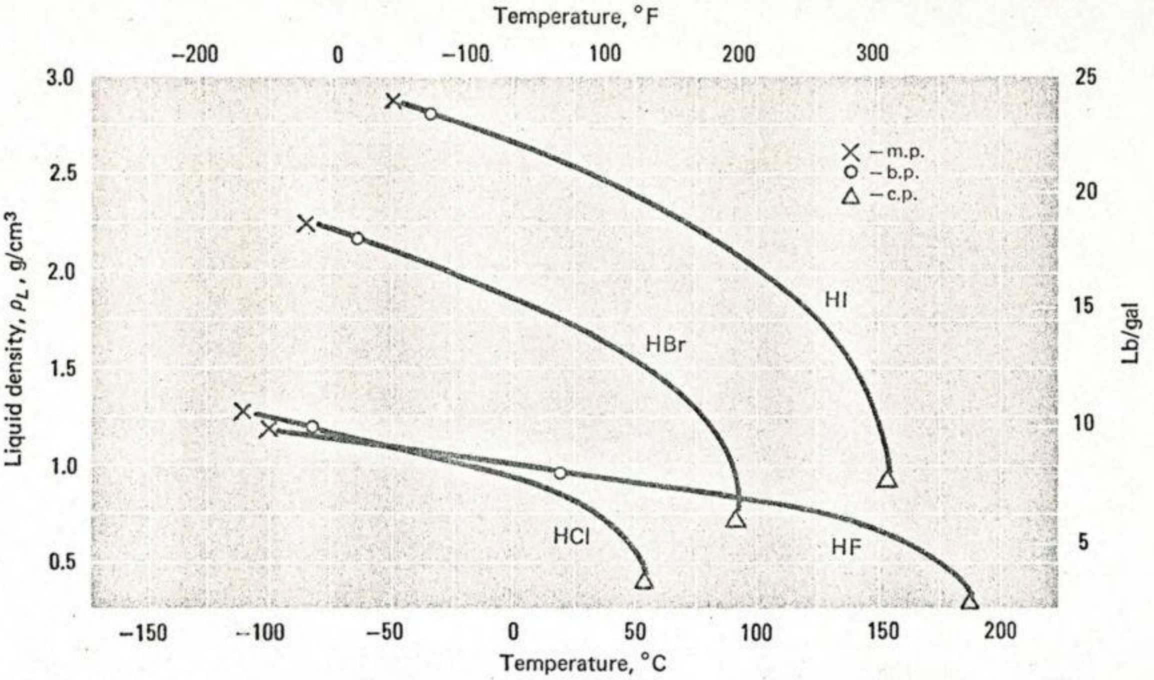
▩ Laboratory data ◪ Laboratory plus correlations ☐ All correlated data

Fig. 5–4	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Hydrogen fluoride	▩	◪	4,10,12,169,184
Hydrogen chloride	◪	☐	12,19
Hydrogen bromide	◪	☐	4,12
Hydrogen iodide	◪	☐	4,164

▩ Laboratory data ◪ Laboratory plus correlations ☐ All correlated data

Liquid Heat Capacity—Fig. 5–4





Liquid Density—Fig. 5–5

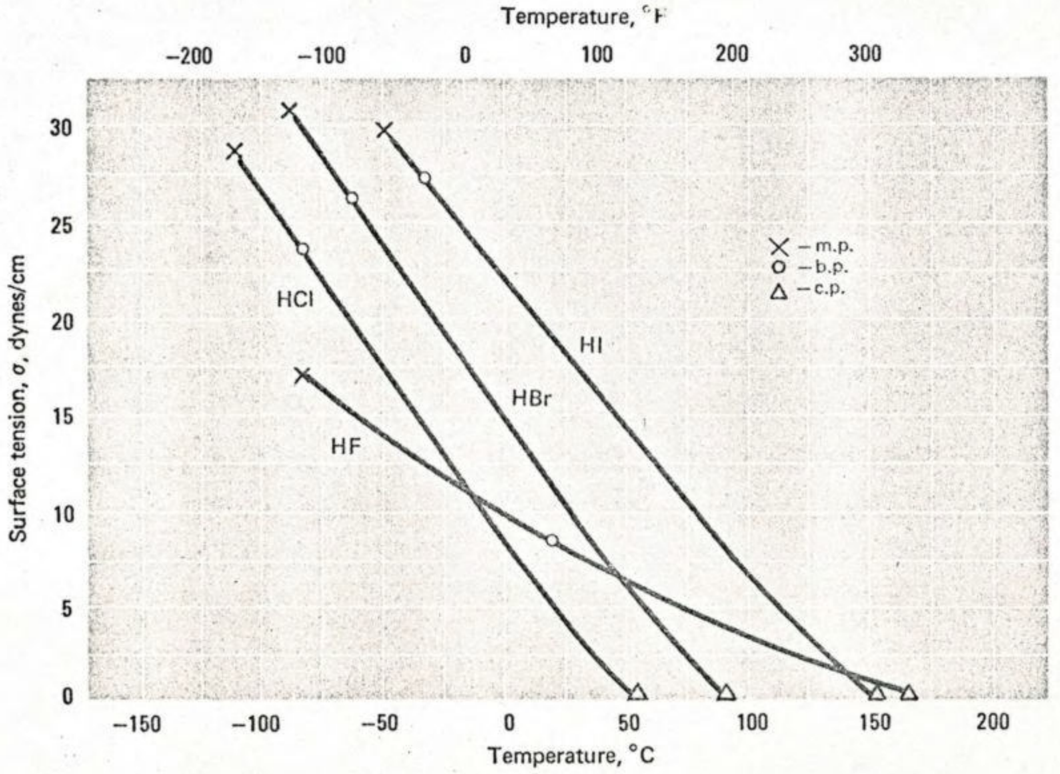
Fig. 5–5	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Hydrogen fluoride	■	■	4, 10, 12, 169, 182, 183
Hydrogen chloride	◪	■	4, 6, 9, 10, 12, 30, 162, 163, 167, 170, 171, 174
Hydrogen bromide	■	◪	4, 6, 10, 12
Hydrogen iodide	■	◪	4, 6, 10, 12, 167, 174

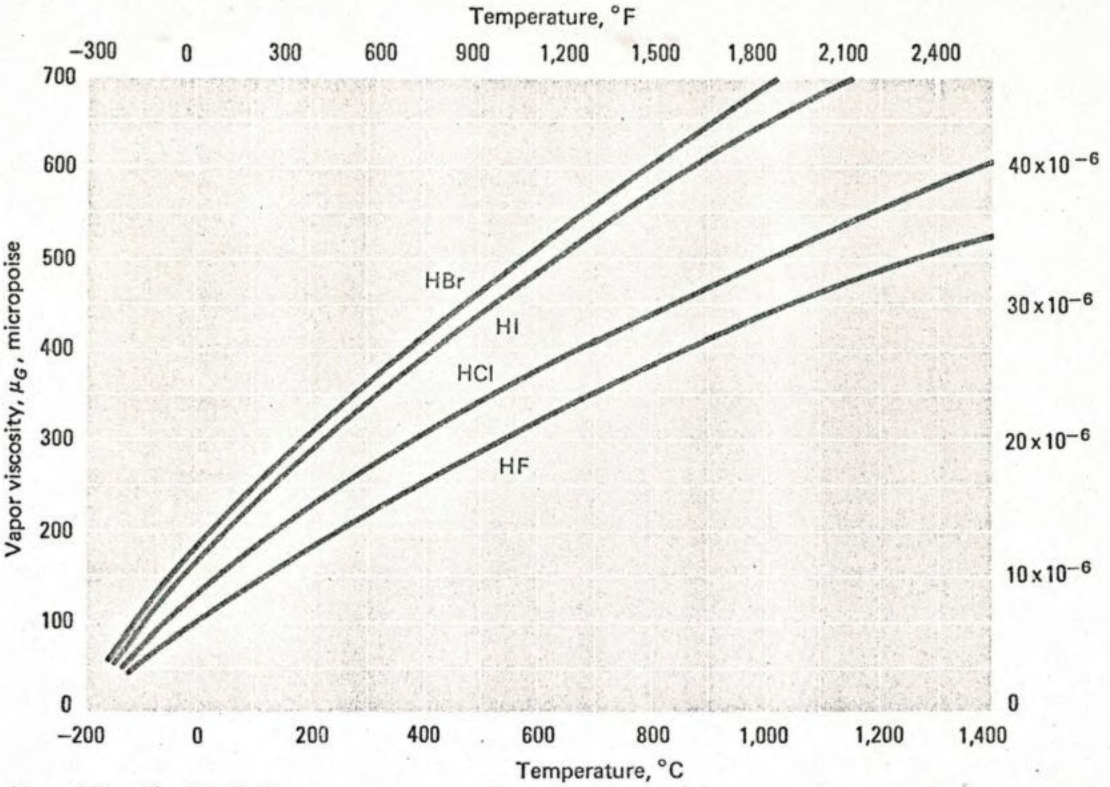
■ Laboratory data ◪ Laboratory plus correlations ☐ All correlated data

Fig. 5–6	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Hydrogen fluoride	■	◪	4, 10, 12, 79, 169
Hydrogen chloride	◪	☐	4, 10, 12, 168
Hydrogen bromide	■	◪	10, 12, 79, 168
Hydrogen iodide	◪	☐	10, 12, 168

■ Laboratory data ◪ Laboratory plus correlations ☐ All correlated data

Surface Tension—Fig. 5–6





Vapor Viscosity—Fig. 5–7

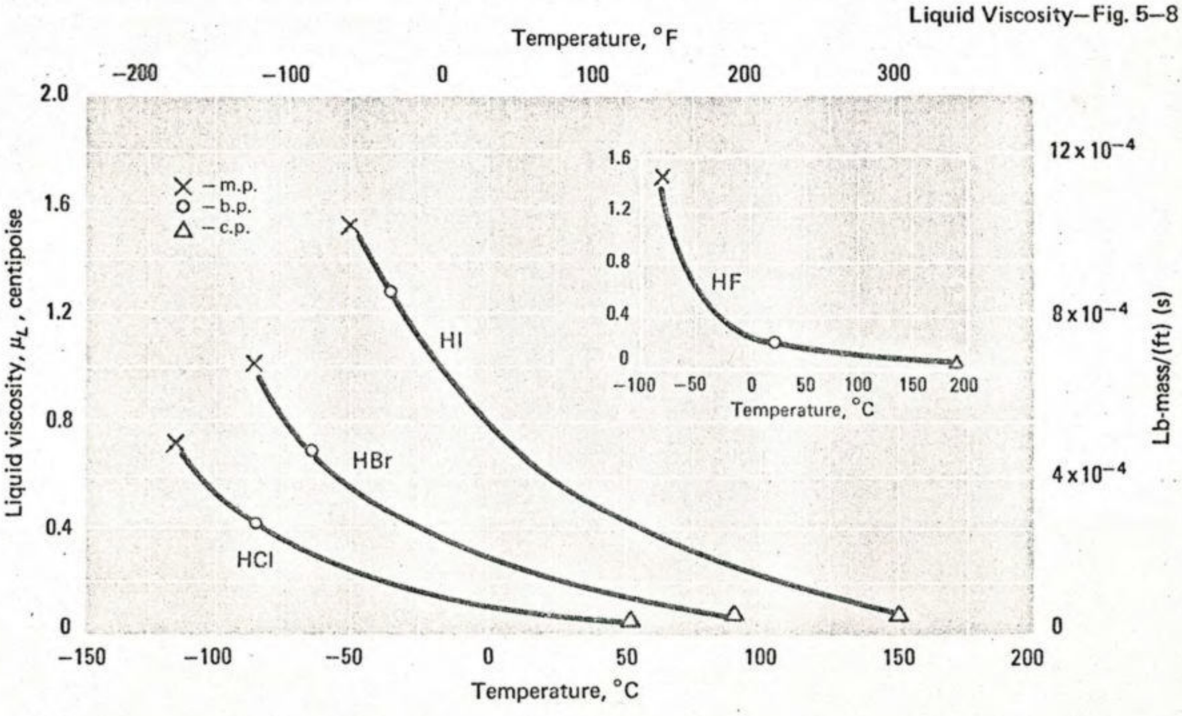
Fig. 5–7	Temperature Range, C			References
	0–500	500–1,000	1,000–1,500	
Hydrogen fluoride	◪	☐	☐	14, 18, 187
Hydrogen chloride	◪	☐	☐	2, 4, 6, 10, 12, 18, 19, 158, 159, 172, 173
Hydrogen bromide	◪	☐	☐	2, 6, 10, 12, 18
Hydrogen iodide	◪	☐	☐	2, 6, 10, 12, 18, 19, 159, 172

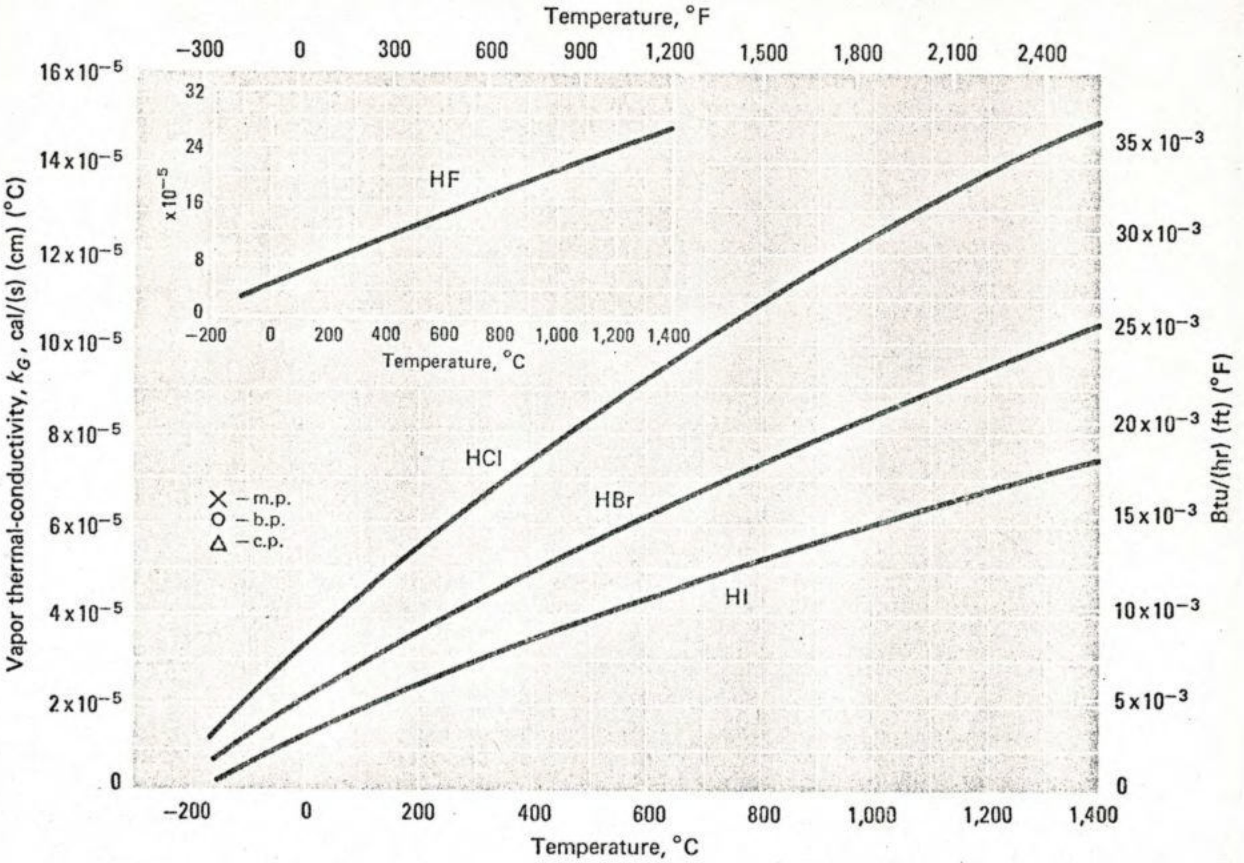
■ Laboratory data ◪ Laboratory plus correlations ☐ All correlated data

Fig. 5–8	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Hydrogen fluoride	◪	☐	10, 12, 169
Hydrogen chloride	◪	◪	12, 165, 168
Hydrogen bromide	◪	☐	12, 168
Hydrogen iodide	◪	☐	12, 168

■ Laboratory data ◪ Laboratory plus correlations ☐ All correlated data

Liquid Viscosity—Fig. 5–8





Vapor Thermal Conductivity—Fig. 5–9

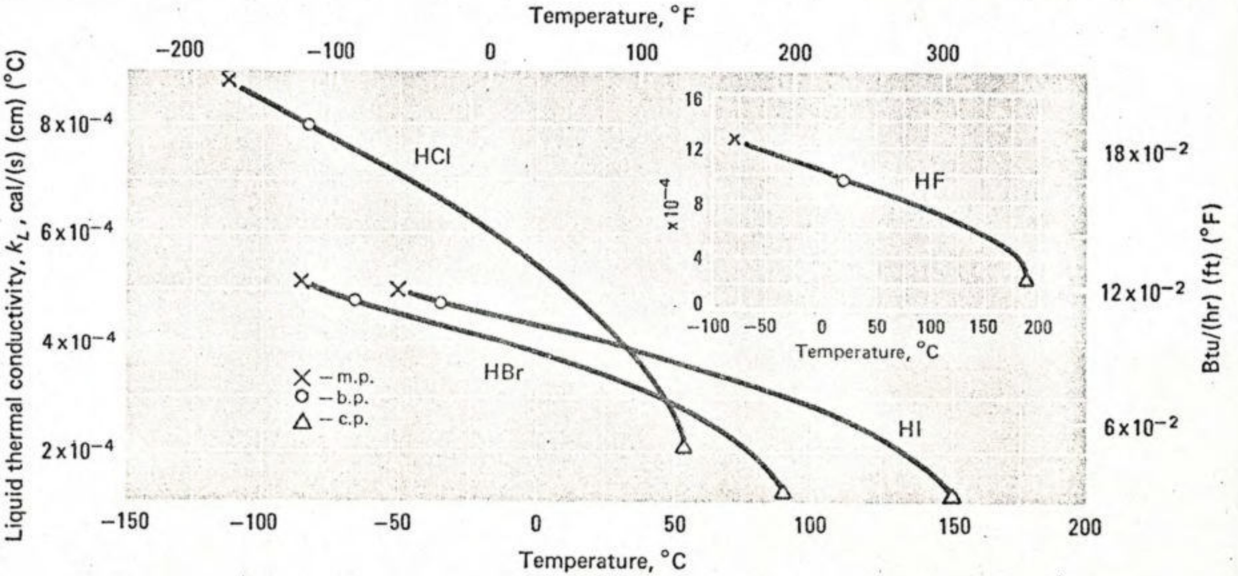
Fig. 5–9	Temperature Range, C			References
	0–500	500–1,000	1,000–1,500	
Hydrogen fluoride	◪	☐	☐	65, 177, 180
Hydrogen chloride	◪	☐	☐	18, 19, 36, 65, 84, 158, 160, 173
Hydrogen bromide	◪	☐	☐	18, 36, 40, 65
Hydrogen iodide	☐	☐	☐	18

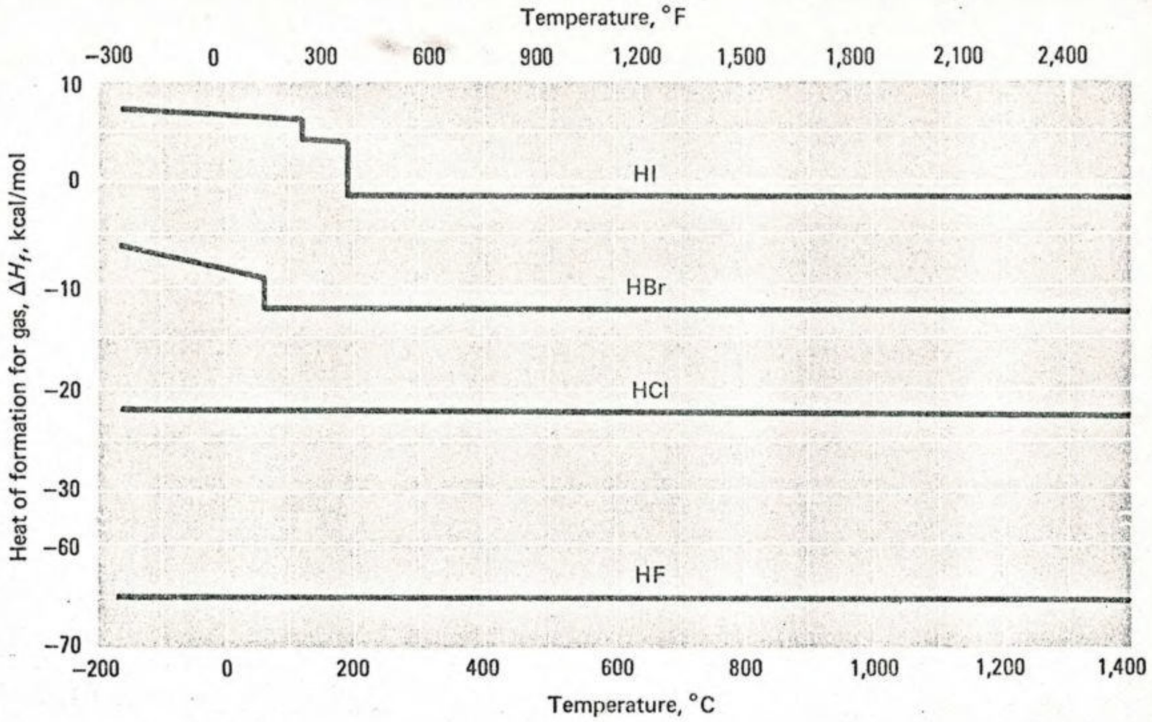
■ Laboratory data ◪ Laboratory plus correlations ☐ All correlated data

Fig. 5–10	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Hydrogen fluoride	☐	☐	13, 14, 65
Hydrogen chloride	☐	◪	14, 65, 173, 175, 176
Hydrogen bromide	☐	☐	14, 65, 173
Hydrogen iodide	☐	☐	14, 65, 173

■ Laboratory data ◪ Laboratory plus correlations ☐ All correlated data

Liquid Thermal Conductivity—Fig. 5–10





Heat of Formation—Fig. 5--11

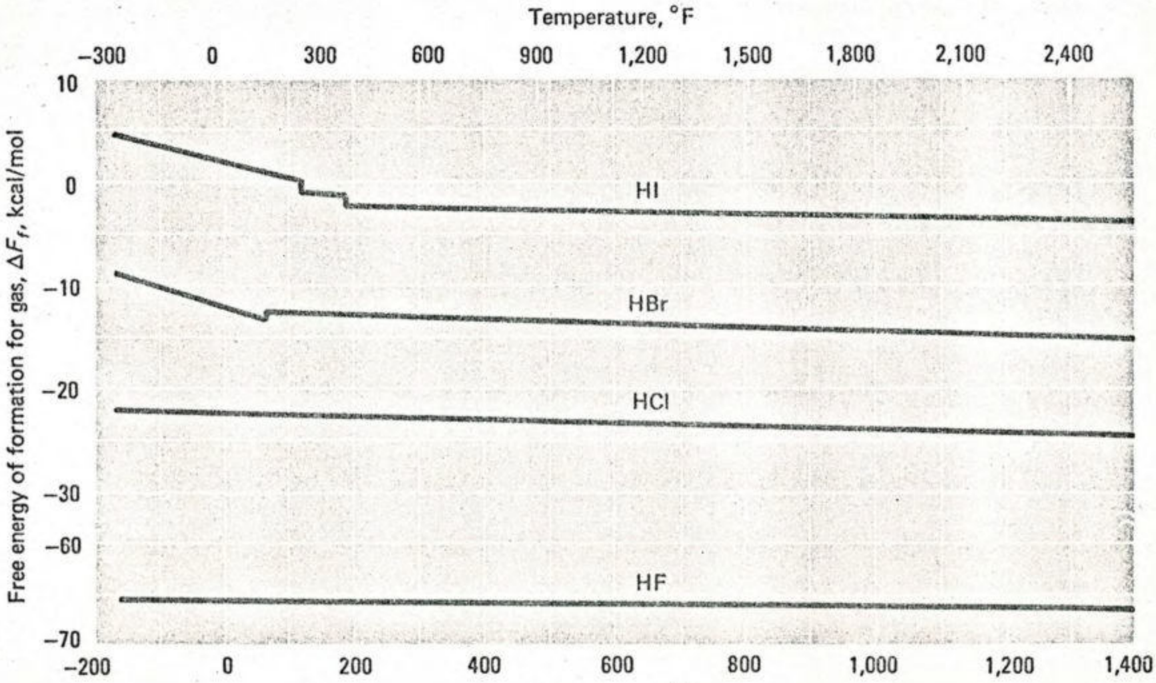
Fig. 5–11	Temperature Range, C			References
	0–500	500–1,000	1,000–1,500	
Hydrogen fluoride	◪	◪	◪	7, 11, 15, 20, 21, 179, 186
Hydrogen chloride	◪	◪	◪	7, 11, 15, 20, 21, 166
Hydrogen bromide	◪	◪	◪	7, 15, 20, 21, 166
Hydrogen iodide	◪	◪	◪	7, 15, 20, 21

■ Laboratory data ◪ Laboratory plus correlations ☐ All correlated data

Fig. 5–12	Temperature Range, C			References
	0–500	500–1,000	1,000–1,500	
Hydrogen fluoride	◪	◪	◪	7, 15, 20, 21
Hydrogen chloride	◪	◪	◪	7, 15, 20, 21
Hydrogen bromide	◪	◪	◪	7, 15, 20, 21
Hydrogen iodide	◪	◪	◪	7, 15, 20, 21

■ Laboratory data ◪ Laboratory plus correlations ☐ All correlated data

Free Energy of Formation—Fig. 5—12



1—4). Computed values agreed well, the average deviation being less than 2.5% for the fluoride, 3% for the chloride and bromide, and 2% for the iodide.

Viscosity—Fig. 5—7, 5—8

For hydrogen fluoride, vapor viscosity was determined from experimental data and the correlation results of Svehla, (Eq. 4—1) [*18,187*].

For the other halides, coverage outside the experimental range was made from correlation results of Svehla, and Thodos and Brebach (Eq. 5—3) [*172*]:

$$\mu_G = \mu_{T_c} f(T_r) \qquad (5\text{—}3)$$

In Eq. (5—3), μ_G = gas viscosity at atmospheric pressure, micropoise: μ_{T_c} = viscosity of the gas at atmospheric pressure and critical temperature, micropoise; $f(T_r) = T_r^{0.979}$ when $T_r \leqq 1$, and $1.196(T_r^{0.659})$ when $T_r \geqq 3.5$; between 1 and 3.5, use original curve [*172*].

Deviations from the best data fitting were less than 5% for hydrogen chloride, 6.5% for hydrogen iodide.

Liquid data for hydrogen fluoride were correlated and extended with the Guzman-Andrade relation (Eq. 1—6). Liquid viscosities from this relation agreed closely with experimental data, deviations being less than 2%.

From the other halides, the full liquid state was covered by modifying the correlation of Brebach and Thodos [*172,173*]:

$$\mu_L = \mu_c f(T_r, P_r) \qquad (5\text{—}4)$$

In Eq. (5—4), μ_c is the viscosity at the critical point; values for $f(T_r, P_r)$ are available for diatomic gases [*173*].

Correlation results compare well with experimental data, average deviations being less than 3.2% for the chloride, 5% for the bromide and 4% for the iodide.

Thermal Conductivity—Fig. 5—9, 5—10

The correlation results of Schaefer and Thodos [*65*], which agree with experimental data (variations being less than 3%), were adopted for thermal conductivities outside the experimental temperature range for hydrogen fluoride, chloride and bromide:

$$k_G = k_c f(T_r, P_r) \qquad (5\text{—}5)$$

In eq. (5—5), k_c is the conductivity at the critical point; $f(T_r, P_r)$ is available from Schaefer and Thodos or Reid and Sherwood [*14*].

The vapor thermal conductivities for hydrogen iodide were based on estimates of Svehla [*18*]. Because experimental data are lacking, the accuracy of the estimates is not known.

For hydrogen chloride and bromide, a comparison of Svehla's estimates with experimental data indicated general agreement, with variations of less than 12% for both. The same agreement was assumed for hydrogen iodide.

Liquid data were found for hydrogen chloride [*175,176*]. For the other halides, the correlation of Schaefer and Thodos was modified [*65,173*]:

$$k_L = k_c f(T_r, P_r) \qquad (5\text{—}6)$$

Values for k_c and $f(T_r, P_r)$ are available [*14,65,173*]. Computed values agreed closely with experimental data, deviations being less than 4.5% for hydrogen chloride.

Heat and Free Energy of Formation—Fig. 5—11, 5—12

Variations in heat of formation values from the best fitting of the data were less than 0.43 kcal/mol for hydrogen fluoride and 0.15 kcal/mol for the other halides.

Free energy deviations for the fluoride, chloride, bromide and iodide were, respectively, less than 0.54, 0.12, 0.37 and 0.13 kcal/mol. #

References

References 1-72 are listed in *Chem. Eng.*, June 10, 1974, p. 78; 73-93, July 8, p. 92; 94-134, Aug. 19, p. 106; 135-157, Sept. 30, p. 122.

158. Andrussow, L., Progress in International Research on Thermodynamic and Transport Properties, 2nd Symposium, ASME, New York, N.Y. (1962), p. 279.
159. Andrussow, L., *Z. Physik. Chem.*, **199**, 314 (1952).
160. Barua, A. K., others, *J. Chem. Phys.*, **49**, 5, 2,422 (1968).
161. Chihara, H., and Nakamura, N., *Bull. Chem. Soc. Japan*, **41**, 8, 1,787 (1968).
162. Franck, E. V. and Mangold, K., *Z. Elektrochem.*, **66**, 260 (1962).
163. Franck, E. V., others, Progress in International Research on Thermodynamic and Transport Properties, 2nd Symposium, ASME, New York, N.Y. (1962), p. 159.
164. Giauque, W. F. and Wiebe, R., *J. ACS*, **51**, 1,441 (1929).
165. Krynicki, K. and Hennel, W., Inst. Nucl. Phys., Cracow, Report. No. 258 (1963).
166. Lacher, J. R., others, *Trans. Faraday Soc.*, **52**, 1,500 (1956).
167. Majumdar, D. K., *Bull. Chem. Soc. Japan*, **40**, 6, 1,541 (1967).
168. McIntosh, D. and Steele, B. D., *Proc. Roy. Soc.*, **73**, 450 (1904).
169. Simons, J. H., "Fluorine Chemistry," Vol. 1, Academic Press, New York, N.Y. (1950).
170. Tans, A.M.P., *Ind. Chemist*, **39**, 11, 597 (1963).
171. Thomas, W., Progress in International Research on Thermodynamic and Transport Properties, 2nd Symposium, ASME, New York, N.Y. (1962), p. 166.
172. Thodos, G. and Breback, W. J., *Ind. Eng. Chem.*, **50**, 7, 1,095 (1958).
173. Thodos, G. and Stiel, L. I., Progress in International Research on Thermodynamic and Transport Properties, 2nd Symposium, ASME, New York, N.Y. (1962), p. 352.
174. Yosim, S. V. and Owens, B. B., *Chem. Phys.*, **39**, 9, 2,222 (1963).
175. Ziebland, H. and Needham, D. P., Proc. of the Fourth Symposium on Thermophysical Properties, ASME, New York, N.Y. (1968), p. 296.
176. Ziebland, H. and Needham, D. P., U. S. Clearinghouse Fed. Sci. Tech. Inform., AD 669683 (1968).
177. Baker, C. E., *J. Chem. Phys.*, **46**, 2,846 (1967).
178. Cole, L. G., others, *J. Chem. Phys.*, **20**, 4, 586 (1952).
179. Feder, H. M., others, *J. Phys. Chem.*, **67**, 1148 (1963).
180. Franck, E. U., and Spalthoff, W., *Naturwissenschaften*, **40**, 580 (1953).
181. Franck, E. U., and Meyer, F., *Z. Elektrochem.*, **63**, 5, 571 (1959).
182. Franck, E. U., and Spalthoff, W., *Z. Physik. Chem.*, **8**, 255 (1956).
183. Franck, E. U. and Spalthoff, W., *Z. Elektrochem.*, **61**, 348 (1957).
184. Hu, J-H, others, *J. ACS*, **75**, 1,232 (1953).
185. Jarry, R. L. and Davis, W., Jr., *J. Phys. Chem.*, **57** 600 (1953).
186. Medvedev, V. A., *Zm. Fiz. Khim.*, **37**, 6, 751 (1963).
187. Posey, J. C., "Viscosity of Gaseous Anhydrous Hydrogen Fluoride", Report K-1063, K-25 Plant, Carbide and Carbon Chem. Co. (Sept. 2, 1953).

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Carl L. Yaws—See *Chem. Eng.*, June 10, p. 78, for biography.