Chemical Engineering

PHYSICAL & THERMODYNAMIC PROPERTIES 1

The Halogens

The physical properties of fluorine, chlorine, bromine and iodine are presented in concise graphs. Scores of experimental determinations plus theoretical correlations are consolidated in one handy spot.

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About the New Series

This is the first of a series of articles that will bring together a wealth of literature data on the physical and thermodynamic properties of important industrial chemicals.

Most data will be presented on large, easy-to-use graphs. Included with the graphs is a key that allows the user to tell at a glance just what portion of each curve is obtained from experimentation, and what portion is deduced from theoretical correlations.

Extensive documentation will be provided. References will be numbered consecutively throughout the series in a running bibliography. The correlations used to extrapolate experimental data are briefly explained. Margins of statistical accuracy are noted where possible.

The first half of the series will cover inorganic materials. In addition to the halogens of this article, upcoming installments will deal with:

- **Nitrogen oxides (N_2O, NO, NO_2).**
- **Sulfur oxides (SO_2, SO_3).**
- **Carbon oxides (CO, CO_2).**
- **Diatomic gases (H_2, O_2, N_2).**
- **Halogen acids.**
- **Inert gases.**
- **Ammonia and hydrazine.**
- **Major non-halogen acids.**
- **Prominent ammonia derivatives.**
- **Hydrogen oxides.**
- **Others.**

The second half will cover selected organics—tentatively including olefins, alcohols, acids, organic chlorides, amines, aldehydes, ketones, aromatic compounds, nonaromatic cyclic compounds and others.

The Halogens

Physical and thermodynamic property data for the halogens—fluorine, chlorine, bromine and iodine—are of special value to engineers in the chemical process industries (CPI). The design and selection of process equipment often requires knowledge of such properties as vapor pressure, critical values, latent heat, heat capacity, density and viscosity.

For the sake of simplicity, all curves relate a specific property to temperature only. Pressure parameters are omitted, and in the case of liquid properties above the normal boiling point, data are limited to the saturation line. This should satisfy the majority of applications. All curves are calibrated in English and metric units.

Explanations of theoretical correlations and average deviations for the data investigated follow.

Critical Values—Table I—I

Critical temperature, pressure and volume have been determined experimentally [*1,2,4,9,10,13,14,43*] for fluorine [64], chlorine [61], bromine [28] and iodine [28]. The reported values are in agreement with only 3% spread. Exceptions to this degree of accuracy are the critical pressure of fluorine, critical volume of bromine, and the critical temperature of iodine. In these latter examples, the deviation is 8-12%.

Heat of Vaporization—Fig. 1—1

The Watson correlation [13,14] was used to augment experimental data over the complete liquid state:

$$\frac{\Delta H_v}{\Delta H_{v_1}} = \left(\frac{T_c - T}{T_c - T_1}\right)^n \qquad (1\text{—}1)$$

where the exponent n may vary slightly with different substances, but in general yields accurate results with a value of $n = 0.38$.

Vapor Pressure—Fig. 1—2

Correlated data use the Cox-Antoine type relation:

$$\log P_v = A - B/(T + C) \qquad (1\text{—}2)$$

where A, B and C are constants for a particular substance and are determined from experimental data. The agreement of both the data from the various sources and the correlation is generally good; deviations from the least-squares fit are less than 5% in most cases.

Heat Capacity—Fig. 1—3, 1—4

Vapor heat capacity data at constant atmospheric pressure (for the ideal gas state) are based primarily on spectroscopic and molecular structure determinations. In general, data agreement is good between the various sources, with differences being less than 3%.

In the case of liquid-heat-capacity (at constant pressure), the data for fluorine cover the full liquid state. For chlorine [43,61,72] and bromine [51], the temperature range has been extended over the full liquid state by differentiating enthalpy-temperature data. For iodine, the liquid heat capacity has been extrapolated using the relationship:

$$C_p \times \rho^n = C \qquad (1\text{—}3)$$

where the exponent, n, is determined from experimental data. With $n = 1/2$, the relationship has shown very good agreement with experimental heat capacities for fluorine (30 data points) and chlorine (10 data points) at only 5% deviation. The extrapolated liquid heat capacities are considered reasonably accurate up to about 80% of the critical temperature.

Density—Fig. 1—5

For chlorine and bromine respectively, temperature ranges for experimental density data are: −70°C to the critical temperature, and from room temperature to critical. The data were extrapolated to account for density at the melting point. Agreement between the various sources is very good, with only a 3% spread.

Surface Tension—Fig. 1—6

To supplement experimental data, surface tension over the full liquid state was determined from the Othmer [53] linear relationship, which equates the log surface tension with the log critical temperature difference:

$$\log \sigma = A + B \log(T_C - T) \qquad (1\text{—}4)$$

A straight line was obtained for the data. Comparison of the computed values with experimental data indicated agreement with only 2% variation for fluorine, bromine and iodine. The variation is less than 3% in the case of chlorine (16 data points).

Viscosity—Fig. 1—7, 1—8

Vapor viscosity over the expanded temperature range was estimated with the Sutherland relation [14]:

$$\mu_G = bT^{3/2}/(S + T) \qquad (1\text{—}5)$$

A straight line was obtained for each halogen upon plotting the ratio $T^{3/2}/\mu_G$ versus T, from which the slope and "Sutherland constant" intercepts were determined. Comparison with the estimates of Svehla [18] show close agreement. Comparison with available data indicate deviations from the least-squares fit of less than 2% for fluorine and chlorine.

Liquid-viscosity was also examined. Upon plotting the data, a straight line for each halogen was obtained for the log viscosity versus reciprocal temperature in accordance with the Guzman-Andrade relationship [13,14]:

$$\log \mu_L = A + (B/T) \qquad (1\text{—}6)$$

Deviations were only 2.1% for fluorine, 2.5% for chlorine, and 3% for bromine.

Thermal Conductivity—Fig. 1—9, 1—10

Thermal conductivity for the vapor has been experimentally measured at low pressures by Franck et al. [36,37]. Additional data for the expanded temperature range were determined from the method of Schaefer and Thodos [14,65], which is based on the corresponding-states behavior and which utilizes the original data of Franck for the correlation constants. Using this method, the thermal conductivity at atmospheric pressure is given in a graphical presentation as a function of temperature, critical temperature and critical conductivity. Agreement with experimental data shows 3.2% maximum deviation [65]. Comparison of the results with other estimation methods indicate an average of 2 to 13% variation for Svehla [18] and 1 to 8% for Liley [19,44].

Liquid-thermal-conductivity data were not identified in the literature screening for fluorine, chlorine and iodine. One source was identified for bromine [63] for data in the 10 to 50°C range. Data for the remaining halogens over the full temperature range were determined by the corresponding-states method of Schaefer and Thodos [14,65]. Average error of 7% was indicated for bromine. Precise accuracy of the values over the full temperature range is not known.

(*Continues through p. 78.*)

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 Halogens

Table I–I

Identification	Fluorine, F_2	Chlorine, Cl_2	Bromine, Br_2	Iodine, I_2
State (std. conditions)	Gas	Gas	Liquid	Solid
Molecular weight	38.00	70.91	159.8	253.8
Boiling point, °C	−188.1	− 34.06	58.78	184.4
Melting point, °C	−219.6	−101.0	− 7.20	113.6
Critical temp., °C	−129.0	144.0	315.0	546.0
Critical pressure, atm	53.0	77.3	102.0	116.0
Critical volume, cm^3/g-mol	66.0	124.5	127.0	155.0
Critical compressibility factor, Z_c	0.296	0.281	0.269	0.268

Fig. 1–1	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Fluorine	◪	◪	1, 4, 9, 10, 14, 43, 70
Chlorine	◪	◪	1, 9, 14, 30, 43, 70
Bromine	◪	◪	1, 4, 9, 14, 43, 70
Iodine	◪	◪	1, 4, 9, 43, 62, 70

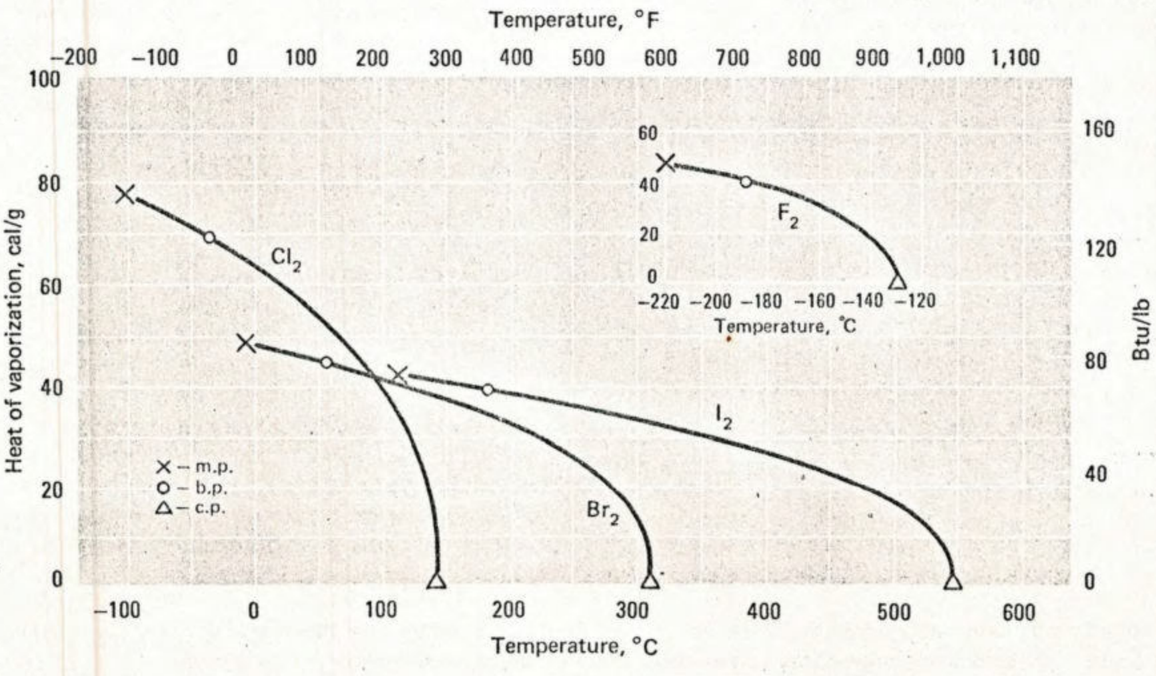
■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Heat of Vaporization—Fig. 1–1

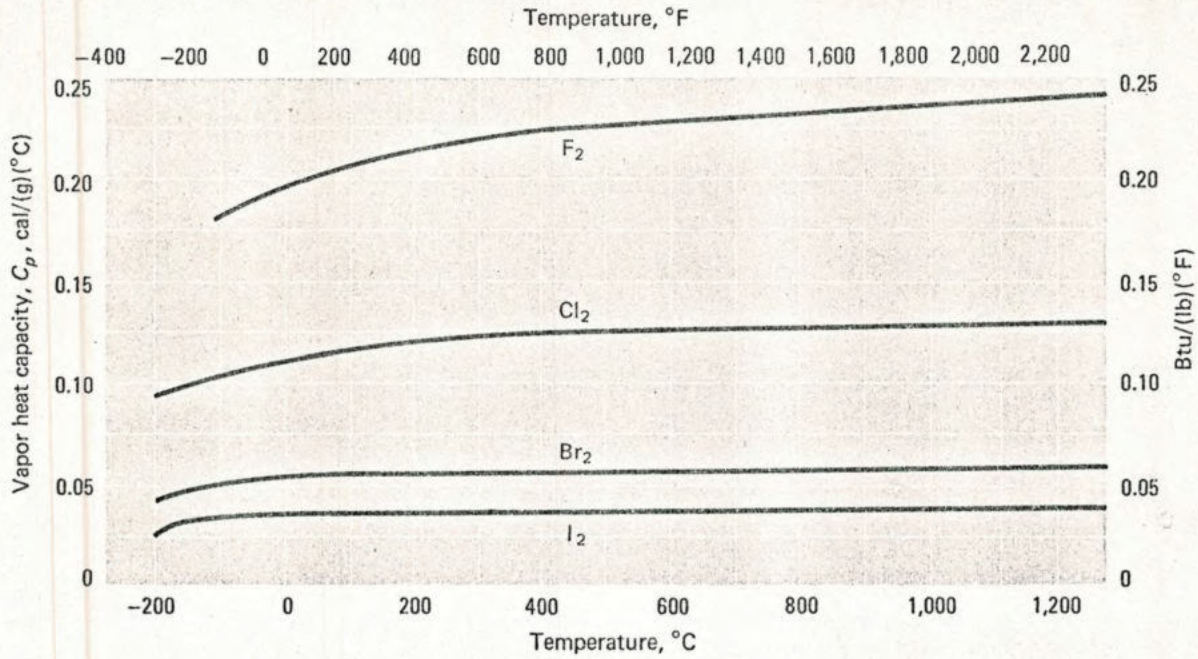
Vapor Pressure—Fig. 1–2 →

Fig. 1–2	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Fluorine	■	■	19, 22, 45, 52, 64, 72
Chlorine	■	■	5, 19, 45, 52
Bromine	■	◪	5, 40, 45, 52
Iodine	■	◪	23, 52

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data



Temperature, °F
-100
0
100
200
300
400
500
600
700
800
900
1,000
10^5
10^4
10^3
10^2
10
1
Vapor pressure, P_v, mm Hg
10^3
10^2
10
1.0
0.1
Psia, lb/in²
Cl_2
Br_2
I_2
F_2
× – m.p.
o – b.p.
Δ – c.p.
-225
-200
-175
-150
-125
Temperature, °C
-100
0
100
200
300
400
500
600
Temperature, °C



Vapor Heat Capacity—Fig. 1–3

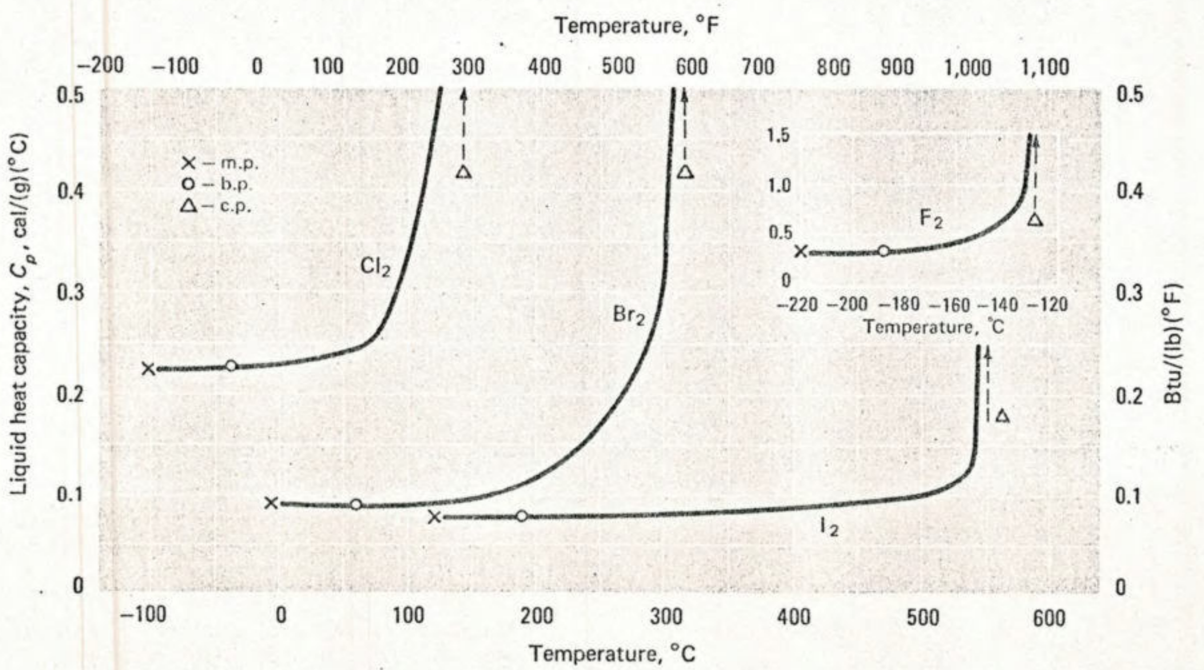
Fig. 1–3	Temperature Range, °C			References
	0–500	500–1,000	1,000–1,500	
Fluorine	◪	◪	◪	7, 8, 11, 12, 15-17, 19, 21, 29, 34, 35, 42, 54-56
Chlorine	◪	◪	◪	7, 8, 11, 12, 15-17, 18-21, 34, 35
Bromine	◪	◪	◪	7, 8, 15-17, 19-21
Iodine	◪	◪	◪	7, 8, 16, 17, 19, 20, 27, 39, 55

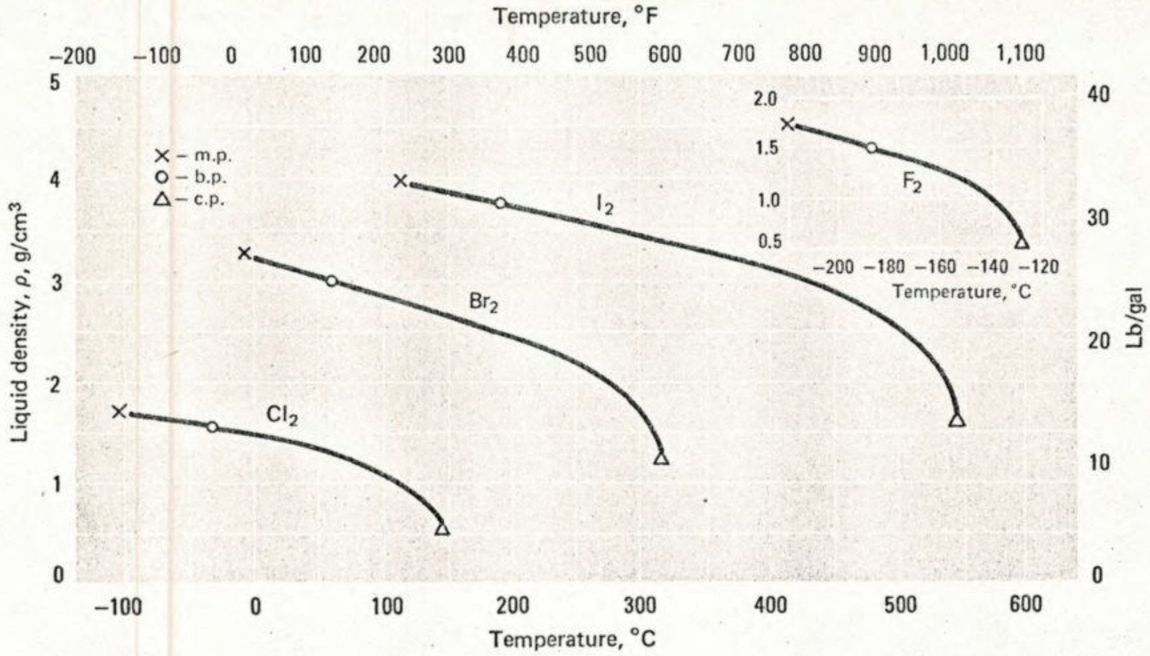
■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Fig. 1–4	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Fluorine	■	■	19, 42, 55, 56
Chlorine	■	◪	19, 32, 44, 61, 71
Bromine	■	◪	4, 19, 43
Iodine	◪	□	4, 19, 43

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Liquid Heat Capacity—Fig. 1–4





Liquid Density—Fig. 1–5

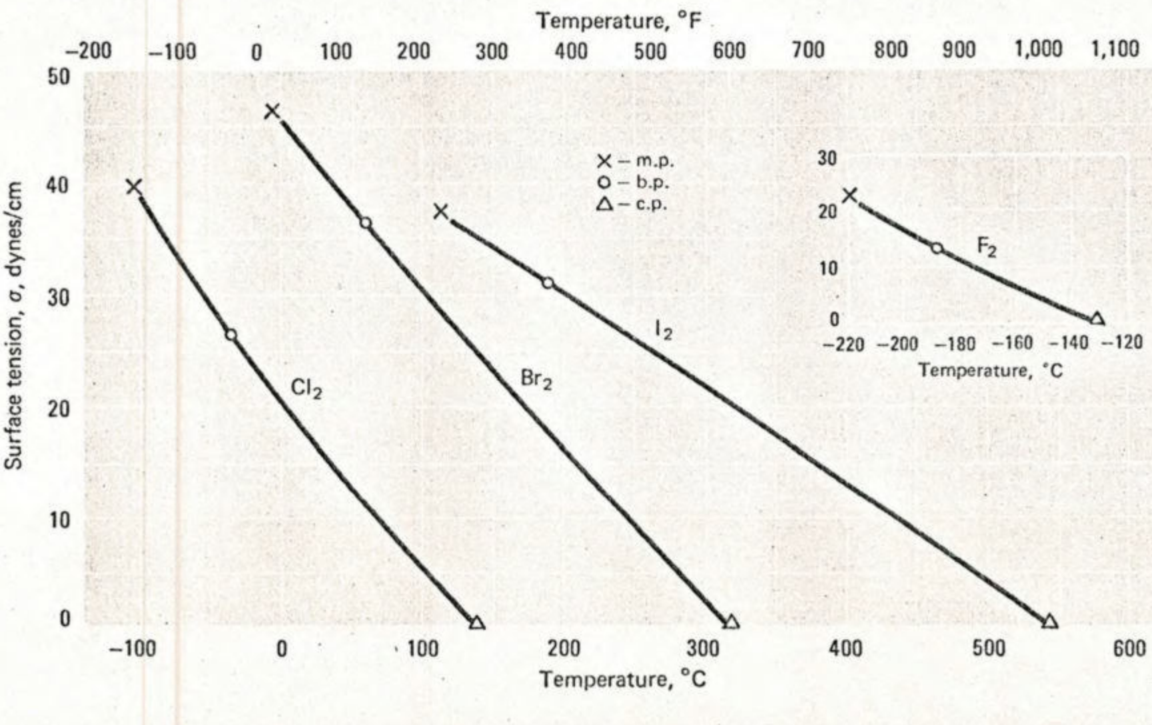
Fig. 1–5	Temperature Range m.p.–b.p.	Temperature Range b.p.–c.p.	References
Fluorine	Laboratory data	Laboratory data	31, 41, 46, 49, 56, 69
Chlorine	Laboratory plus correlations	Laboratory data	1, 4, 43, 71
Bromine	Laboratory plus correlations	Laboratory data	1, 4, 14, 28, 43
Iodine	Laboratory data	Laboratory data	1, 4, 14, 28, 43

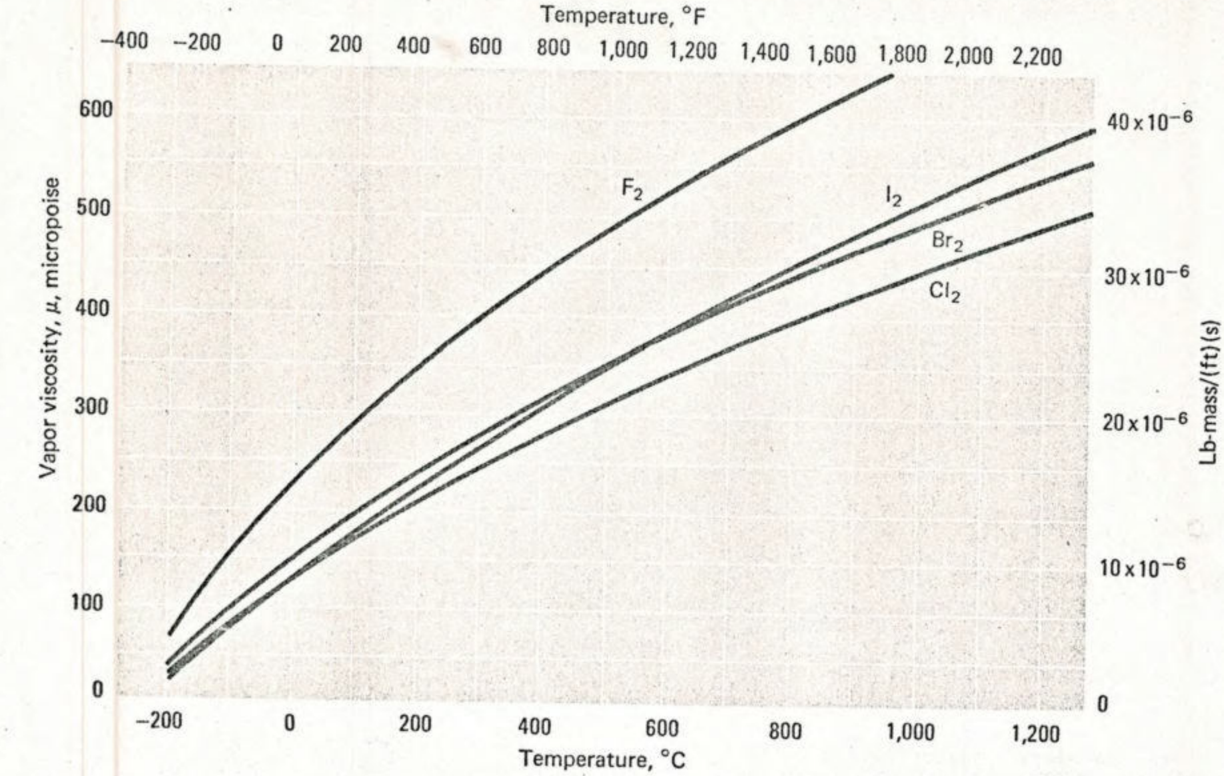
■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Fig. 1–6	Temperature Range m.p.–b.p.	Temperature Range b.p.–c.p.	References
Fluorine	Laboratory plus correlations	All correlated data	31, 69
Chlorine	Laboratory plus correlations	Laboratory plus correlations	2, 6, 9, 33, 43, 61
Bromine	Laboratory plus correlations	All correlated data	2, 6, 9, 43, 63
Iodine	Laboratory plus correlations	All correlated data	50

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Surface Tension—Fig. 1–6





Vapor Viscosity—Fig. 1–7

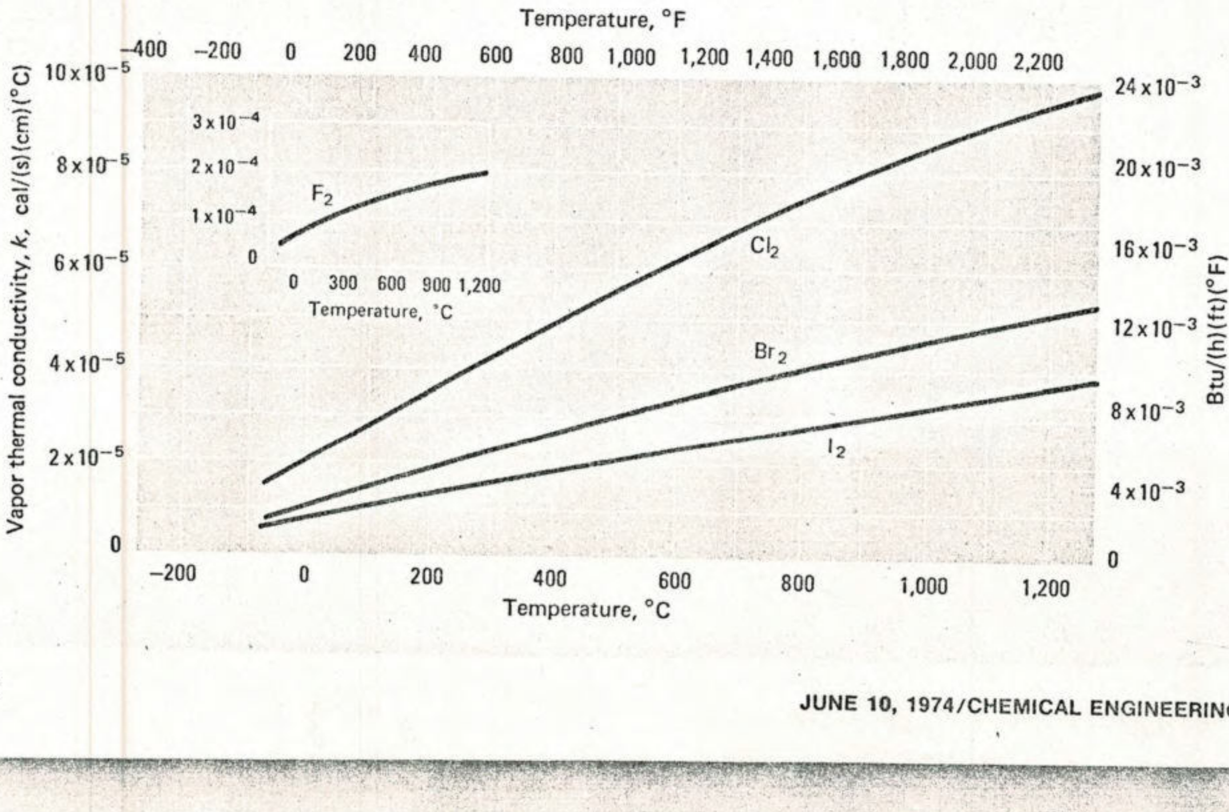
Fig. 1–7	Temperature Range, °C 0–500	500–1,000	1,000–1,500	References
Fluorine	Laboratory plus correlations	All correlated data	All correlated data	19, 38, 47, 48
Chlorine	Laboratory plus correlations	All correlated data	All correlated data	19, 24, 26, 58, 61, 66, 67, 68
Bromine	Laboratory plus correlations	All correlated data	All correlated data	19, 25, 57, 59
Iodine	Laboratory plus correlations	All correlated data	All correlated data	19, 26, 59, 60

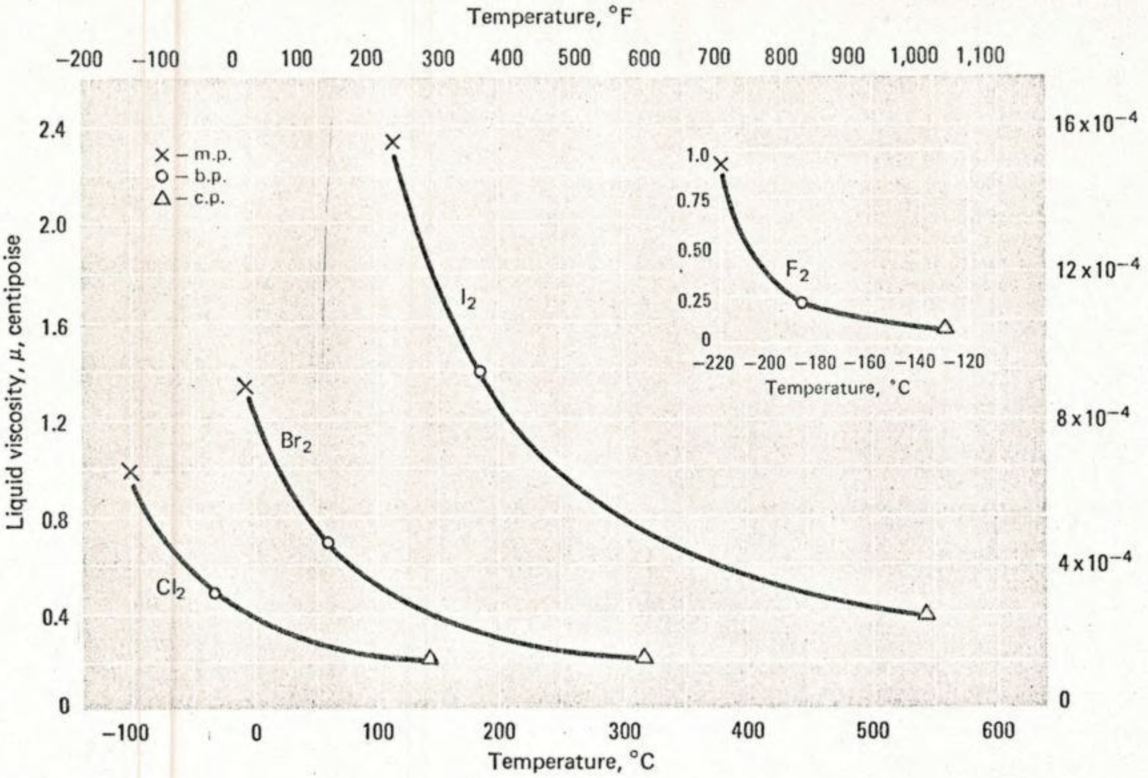
■ Laboratory data ◩ Laboratory plus correlations □ All correlated data

Fig. 1–9	Temperature Range, °C 0–500	500–1,000	1,000–1,500	References
Fluorine	Laboratory data	Laboratory plus correlations	All correlated data	14, 18, 19, 36, 37, 44, 65
Chlorine	Laboratory plus correlations	All correlated data	All correlated data	14, 18, 19, 36, 37, 44, 65
Bromine	Laboratory data	Laboratory plus correlations	All correlated data	14, 18, 19, 36, 37, 44, 65
Iodine	Laboratory plus correlations	All correlated data	All correlated data	14, 18, 19, 36, 37, 44, 65

■ Laboratory data ◩ Laboratory plus correlations □ All correlated data

Vapor Thermal Conductivity—Fig. 1–9





Liquid Viscosity—Fig. 1–8

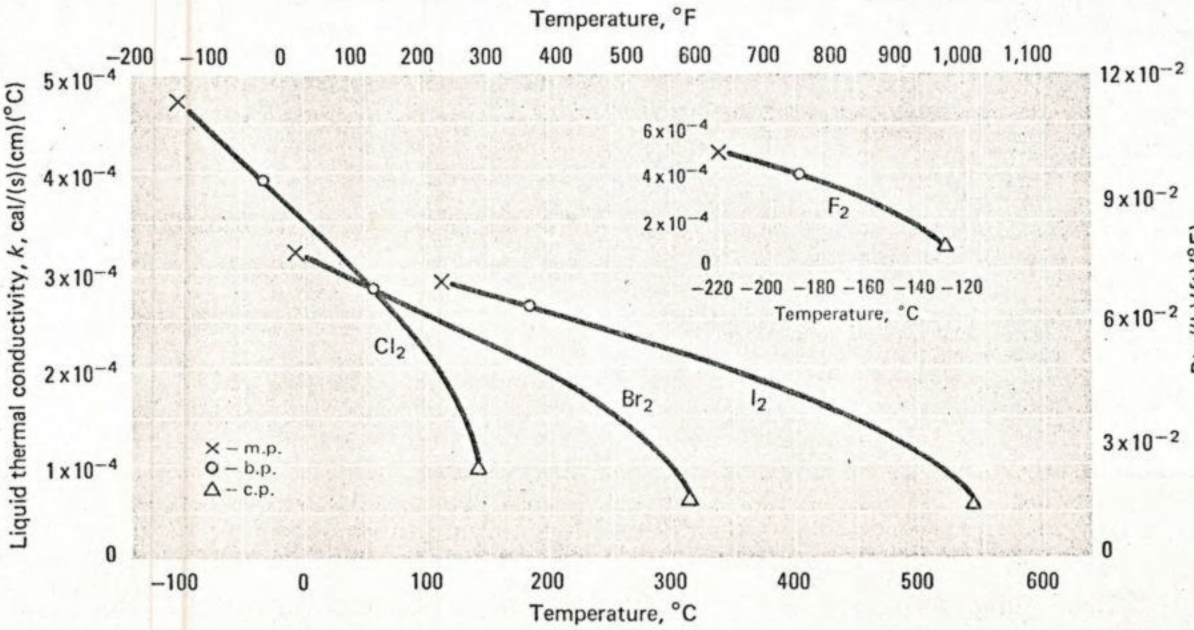
Fig. 1–8	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Fluorine	◪	□	31, 47
Chlorine	◪	◪	2, 4, 61
Bromine	◪	□	2, 3, 9
Iodine	◪	◪	6, 43

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Fig. 1–10	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Fluorine	□	□	14, 65
Chlorine	□	□	14, 65
Bromine	◪	□	14, 63, 65
Iodine	□	□	14, 65

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Liquid Thermal Conductivity—Fig. 1–10



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