21

Methyl chloride, methylene chloride, chloroform and carbon tetrachloride

This month's segment presents physical and thermodynamic data for these widely used chloromethanes.

Carl L. Yaws, Lamar University

☐ The chloromethanes are important to the chemical process industries. Methyl chloride is used to manufacture silicones, butyl rubber, tetramethyl lead and certain specialty chemicals. Methylene chloride is a superior paint stripper for many industrial and home applications; it is also used as a cleaning solvent and heat-transfer medium. Chloroform and carbon tetrachloride are the basic feedstocks for producing air-conditioning refrigerants and aerosol propellants; they also contribute to making general-purpose solvents and specialty chemicals.

Critical Properties—Table 21—1

Experimental data on critical properties are available for all the chloromethanes [*4,416,418,574,637,646,693,706,708,712,715,717,718,721*] except methylene chloride, for which data on critical volume are not obtainable. There is good agreement among the selected reported values. Average deviations proved to be 0.31, 0.34 and 1.3% for critical temperature, pressure and volume.

Critical volume for methylene chloride was estimated by the Lydersen method (Eq. 16—3)*. Applying the method to other chloromethanes produced favorable agreement between predicted and experimental values. Average deviations were less than 1.7% for methyl chloride, chloroform and carbon tetrachloride.

Heat of Vaporization—Fig. 21—1

Experimental data for heat of vaporization were extended with the Watson correlation (Eq. 1—1) to achieve full coverage of the liquid phase. Results from the various sources agree closely; deviations in most cases are less than 1%.

Vapor Pressure—Fig. 21—2

Extensive vapor-pressure data for each chloromethane were correlated over the entire saturated-liquid range with the Cox-Antoine relation (Eq. 1—2). Results from the various investigators are in close agreement.

Heat Capacity—Fig. 21—3, 21—4

Heat capacity data for the ideal gases at low pressure are available for each chloromethane. The recent results

(*text continues on p. 89*)

*See Part 1 of this series for equations starting with a boldfaced numeral "1", Part 2 for those with "2", etc. Table on p. 115 of the Jan. 19, 1976 issue (Part 17) lists publication dates of parts 1 through 16. Parts 18, 19 and 20 appeared in the Mar. 1, Apr. 12 and June 7 issues.

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:

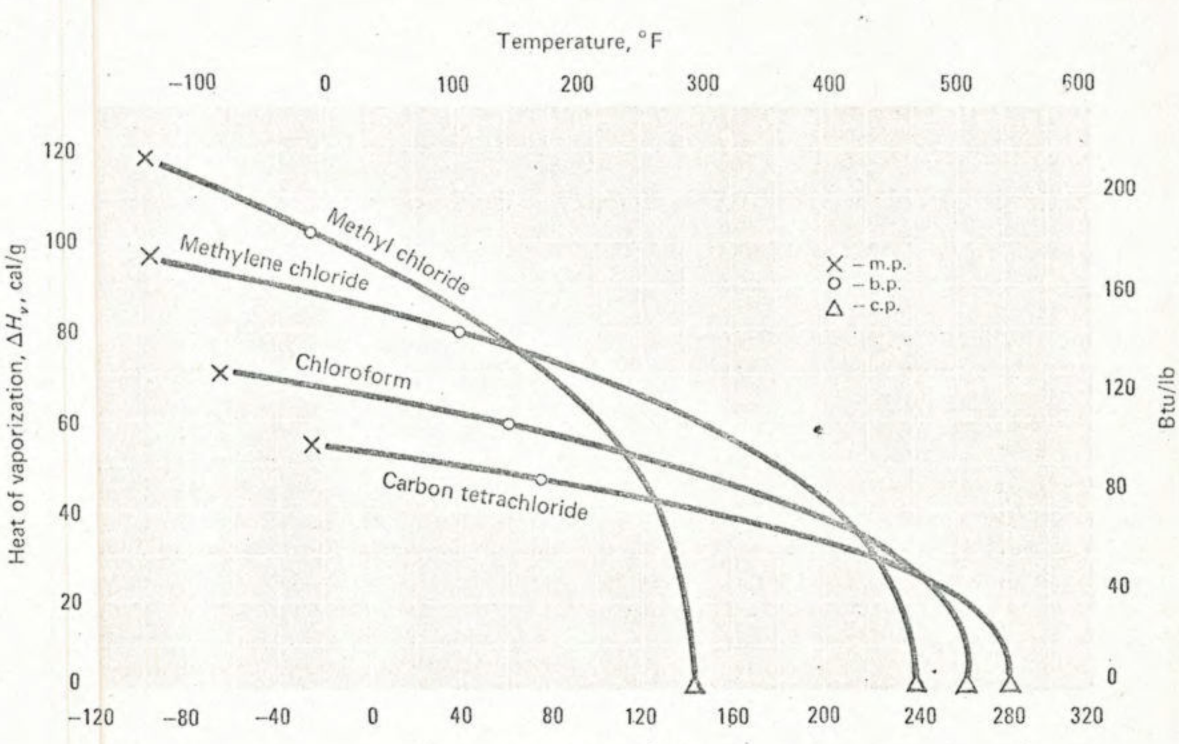
- ▩ Data in this region are experimentally known.
- ◩ Experimental and correlated data used.
- ☐ All data in this region are correlated.

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 chloromethanes — Table I

Identification	Methyl chloride CH_3Cl	Methylene chloride CH_2Cl_2	Chloroform $CHCl_3$	Carbon tetrachloride CCl_4
State (std. conditions)	Gas	Liquid	Liquid	Liquid
Molecular weight, M	50.49	84.93	119.4	153.8
Boiling point, T_b, °C	−23.8	39.8	61.3	76.7
Melting point, T_m, °C	−97.7	−96.7	−63.2	−22.9
Critical temp., T_c, °C	143.1	241.0	263.4	283.2
Critical pressure, P_c, atm	65.9	60.5	54.0	45.0
Critical volume, V_c, cm^3/g-mol	139.1	193.0*	240.0	275.0
Critical compressibility factor, Z_c	0.268	0.277*	0.294	0.271

*Estimated



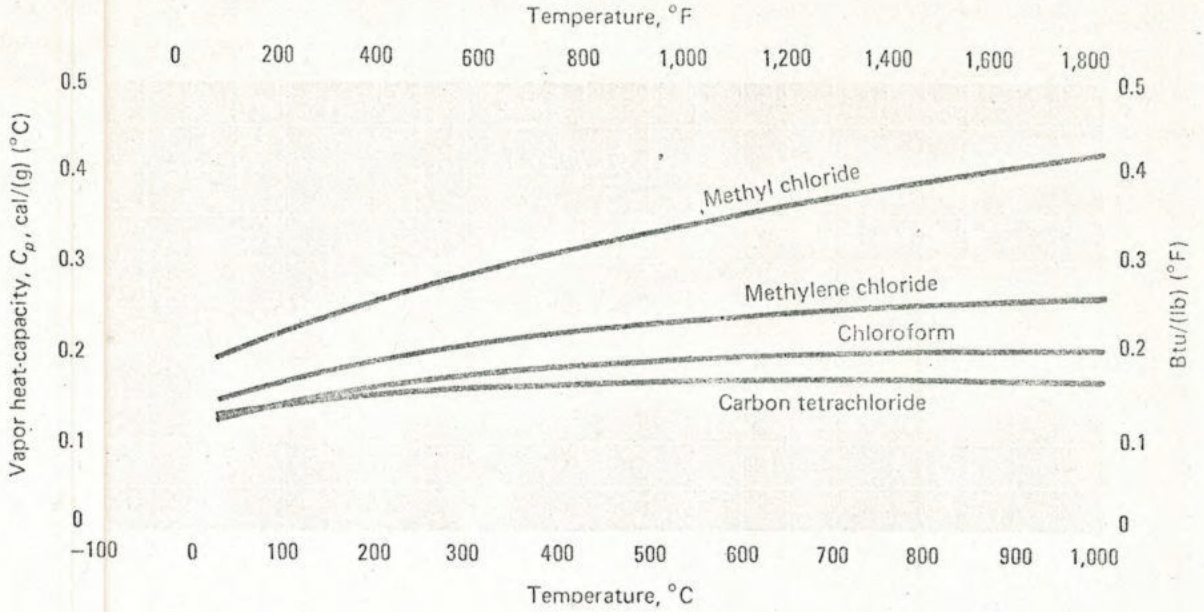
Heat of vaporization — Fig. 1

Fig. 21−1	Temperature range, °C		Reference
	m.p.−b.p.	b.p.−c.p.	
Methyl chloride	◩	◩	4,9,15,574,708,712,718,725
Methylene chloride	◩	◩	4,9,15,574,708,718,721
Chloroform	◩	◩	4,9,15,574,708,718,721
Carbon tetrachloride	◩	◩	4,9,15,574,708,718,721

Vapor pressure — Fig. 2

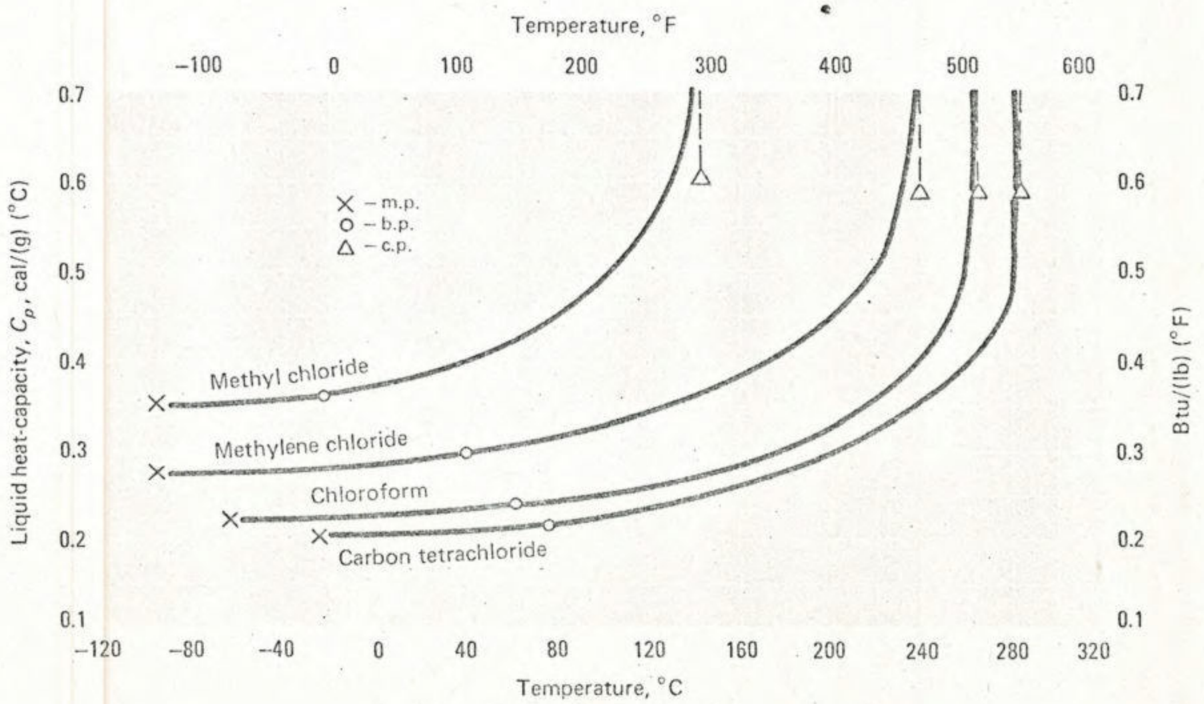
Fig. 21−2	Temperature range, °C		Reference
	m.p.−b.p.	b.p.−c.p.	
Methyl chloride	◩	▩	3,4,6,9,415,416,418,529,548,637,646, 708,712,715
Methylene chloride	◩	◩	3,4,6,415,416,418,529,548,637,708
Chloroform	◩	▩	3,4,6,415,416,529,546,637,708
Carbon tetrachloride	▩	▩	3,4,6,9,415,416,529,548,637,646,708

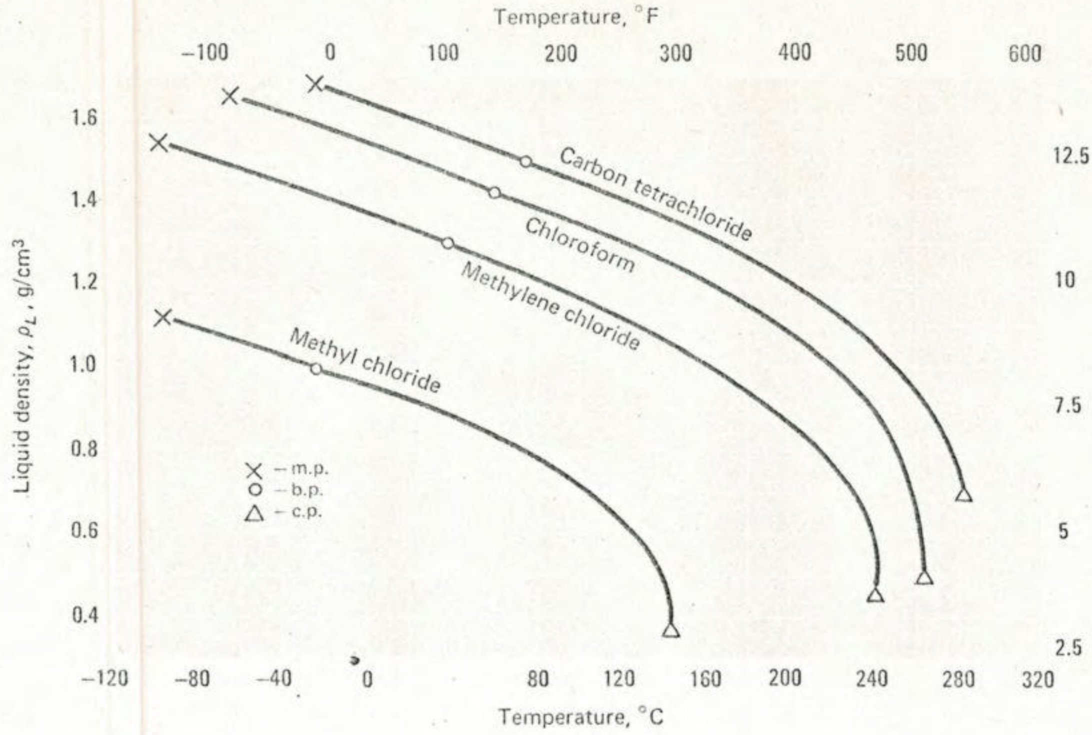

Temperature, °F
−200
−100
0
100
200
300
400
500
600
10^5
10^4
10^3
10^2
10
1
0.1
0.01
Vapor pressure, P_V, mm Hg
10^3
10^2
10
1
10^{-1}
10^{-2}
10^{-3}
Psia
Methyl chloride
Methylene chloride
Chloroform
Carbon tetrachloride
× – m.p.
o – b.p.
△ – c.p.
−160
−120
−80
−40
0
40
80
120
160
200
240
280
320
Temperature, °C



Vapor heat capacity			Fig. 3
Fig. 21–3	Temperature range, °C		Reference
	0–500	500–1,000	
Methyl chloride	☑	☑	7,15,18,19,418,637,714,715,727
Methylene chloride	☑	☑	7,15,18,418,637,714,715,727
Chloroform	☑	☑	15,18,19,418,637,714,715,727
Carbon tetrachloride	☑	☑	15,18,19,418,637,714,715,727

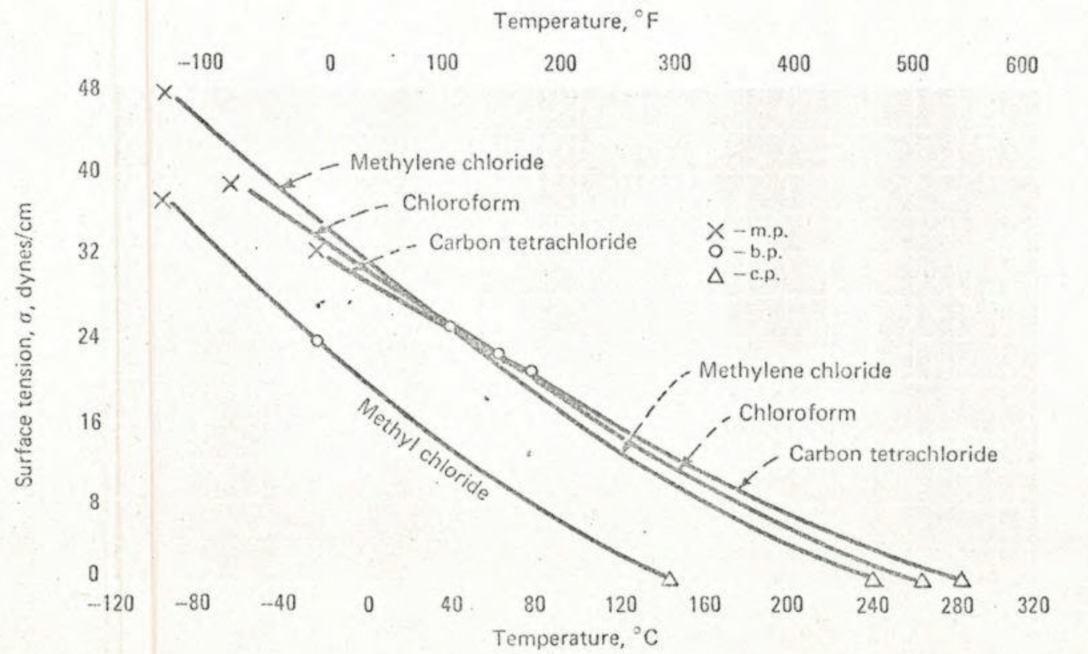
Liquid heat capacity			Fig. 4
Fig. 21–4	Temperature range, °C		Reference
	m.p.–b.p.	b.p.–c.p.	
Methyl chloride	☑	☑	4,19,646,708,717
Methylene chloride	☑	☐	4,6,415,708,717,721
Chloroform	☑	☑	4,6,19,415,416,708,717,721
Carbon tetrachloride	☑	☐	4,6,19,415,416,646,708,717,721

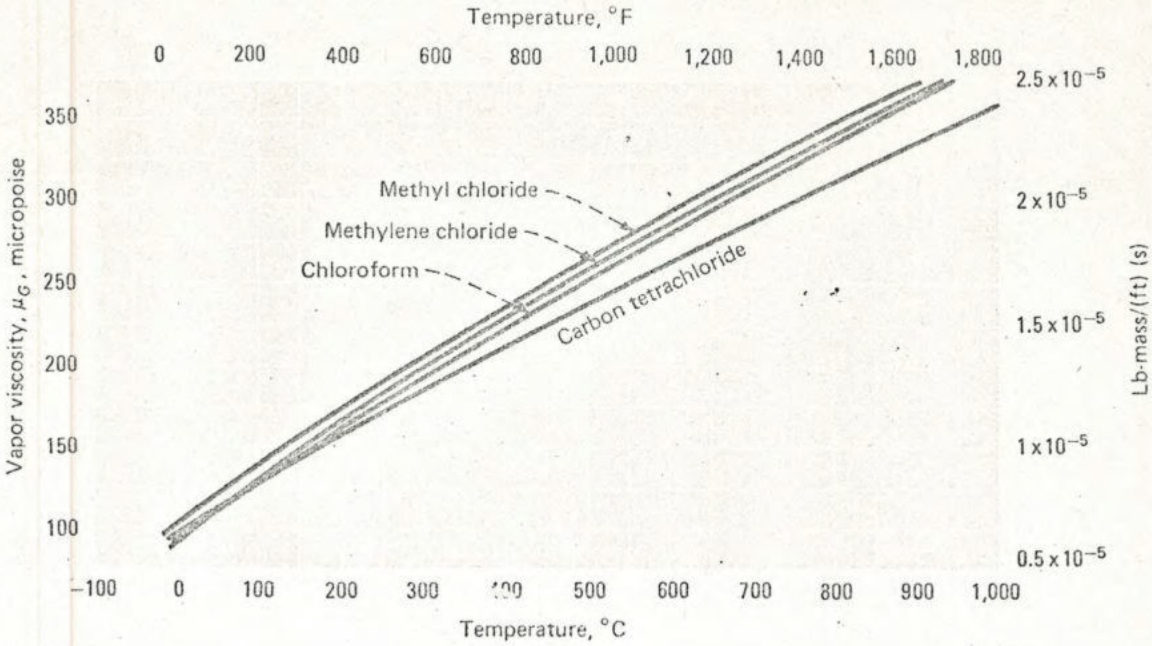




Liquid density			Fig. 5
Fig. 21–5	Temperature range, °C		Reference
	m.p.–b.p.	b.p.–c.p.	
Methyl chloride	◪	▦	4,6,9,415,418,637,646,708,712,718,733
Methylene chloride	◪	◪	4,415,418,637,708,718,719,721,729, 732,733
Chloroform	◪	◪	4,415,418,637,708,718,721,730,733,734
Carbon tetrachloride	◪	▦	4,6,9,415,418,637,646,708,710,718,719, 721,731,733

Surface tension			Fig. 6
Fig. 21–6	Temperature range, °C		Reference
	m.p.–b.p.	b.p.–c.p.	
Methyl chloride	□	◪	4,6,9,79,574,
Methylene chloride	◪	□	4,6,415,637,708,717,721
Chloroform	◪	◪	4,6,9,79,415,574,637,708,717,721
Carbon tetrachloride	◪	◪	4,6,9,79,415,574,637,708,717,721



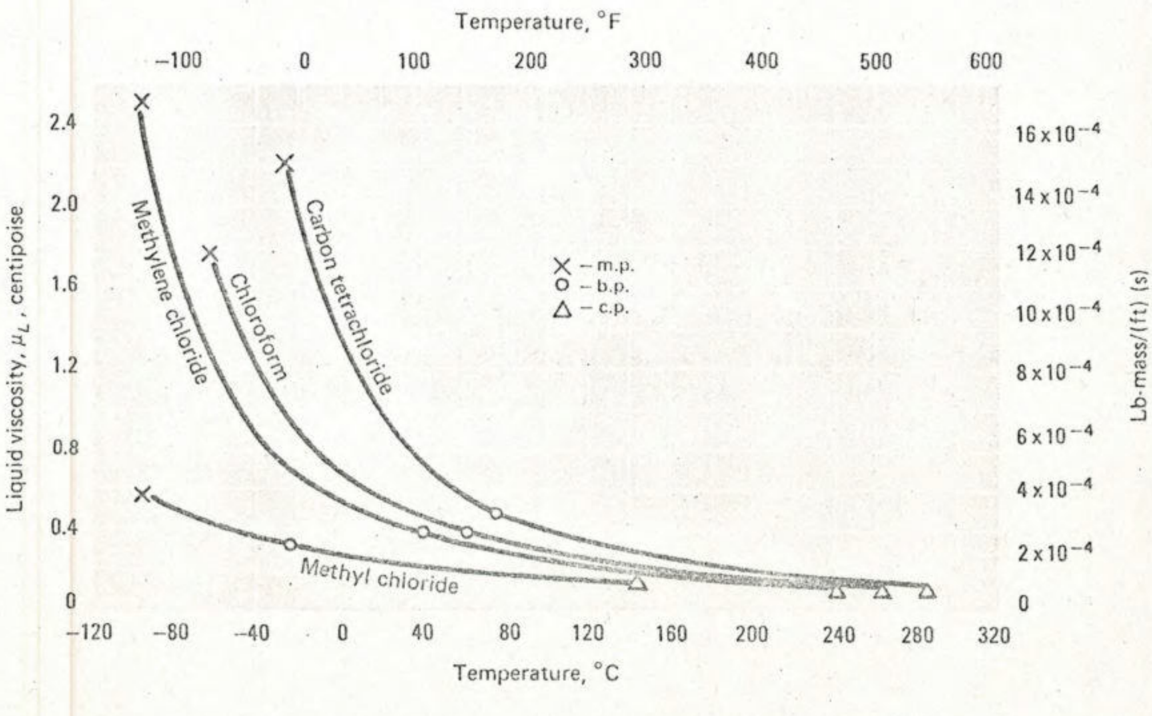


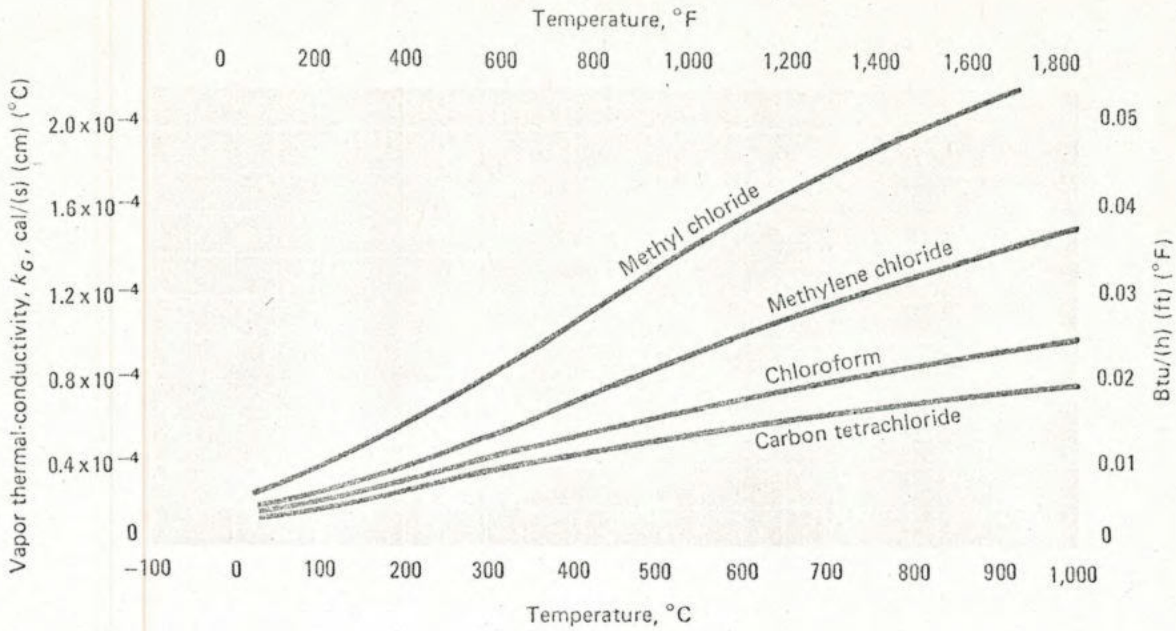
Vapor viscosity — Fig. 7

Fig. 21–7	Temperature range, °C		Reference
	0–500	500–1,000	
Methyl chloride	☑	☐	9,416,467,574,637,646,703,715,716
Methylene chloride	☑	☐	467,637
Chloroform	☑	☐	9,467,574,637,703,715,716
Carbon tetrachloride	☑	☐	416,467,637,646,703,715,716,719,723

Liquid viscosity — Fig. 8

Fig. 21–8	Temperature range, °C		Reference
	m.p.–b.p.	b.p.–c.p.	
Methyl chloride	☑	☑	4,646,703,708,717,728
Methylene chloride	☑	☐	4,6,9,415,416,574,708,717,719,721,728
Chloroform	☑	☐	4,6,9,415,416,467,574,705,708,717,721, 724,728
Carbon tetrachloride	☑	☑	4,6,9,415,416,574,646,708,709,713,717, 719,721,726,728



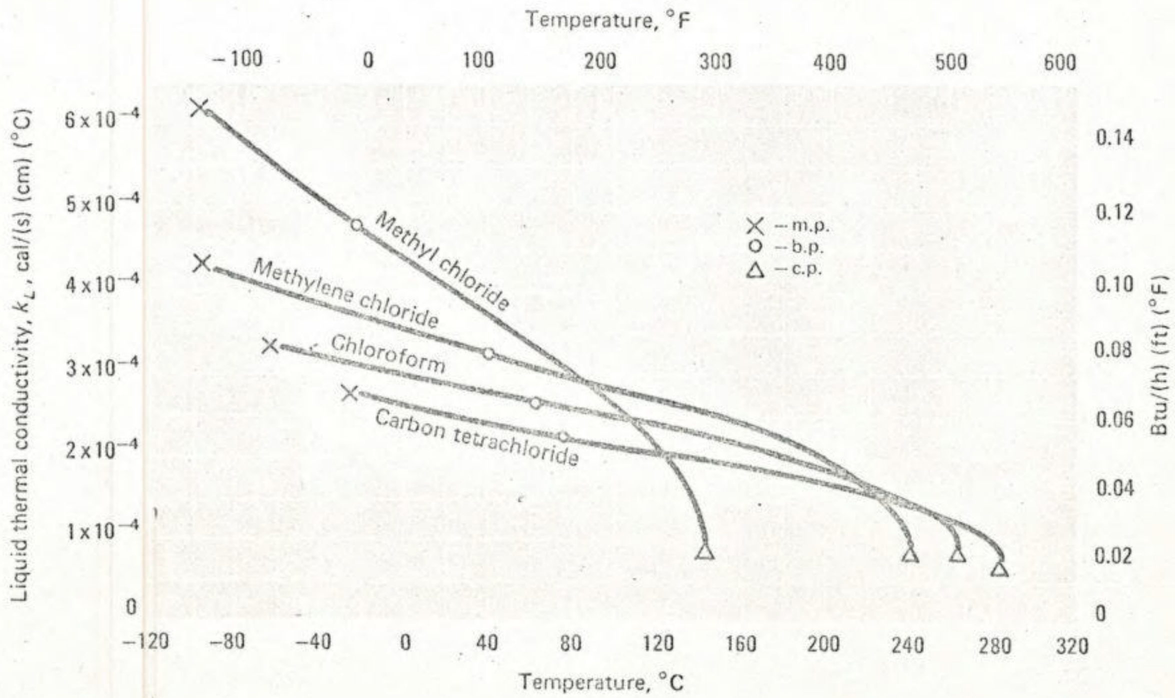


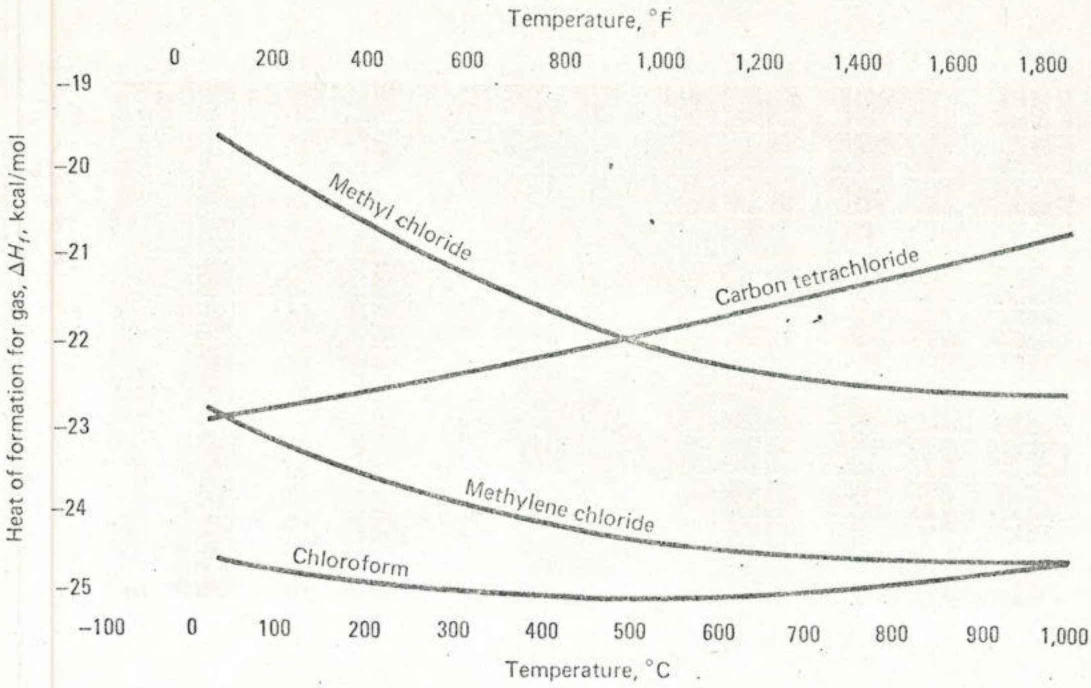
Vapor thermal conductivity — Fig. 9

Fig. 21–9	Temperature range, °C		Reference
	0–500	500–1,000	
Methyl chloride	☑	☐	9,19,84,574,590,625,637
Methylene chloride	☑	☐	625,637
Chloroform	☑	☐	9,19,574,587,590,637
Carbon tetrachloride	☑	☐	9,19,84,574,637,645

Liquid thermal conductivity — Fig. 10

Fig. 21–10	Temperature range, °C		Reference
	m.p.–b.p.	b.p.–c.p.	
Methyl chloride	☑	☑	19,637,708,717
Methylene chloride	☑	☐	481,637,708,717
Chloroform	☑	☑	9,19,481,532,637,708,717
Carbon tetrachloride	☑	☑	9,19,475,481,532,540,637,646,707, 708,717



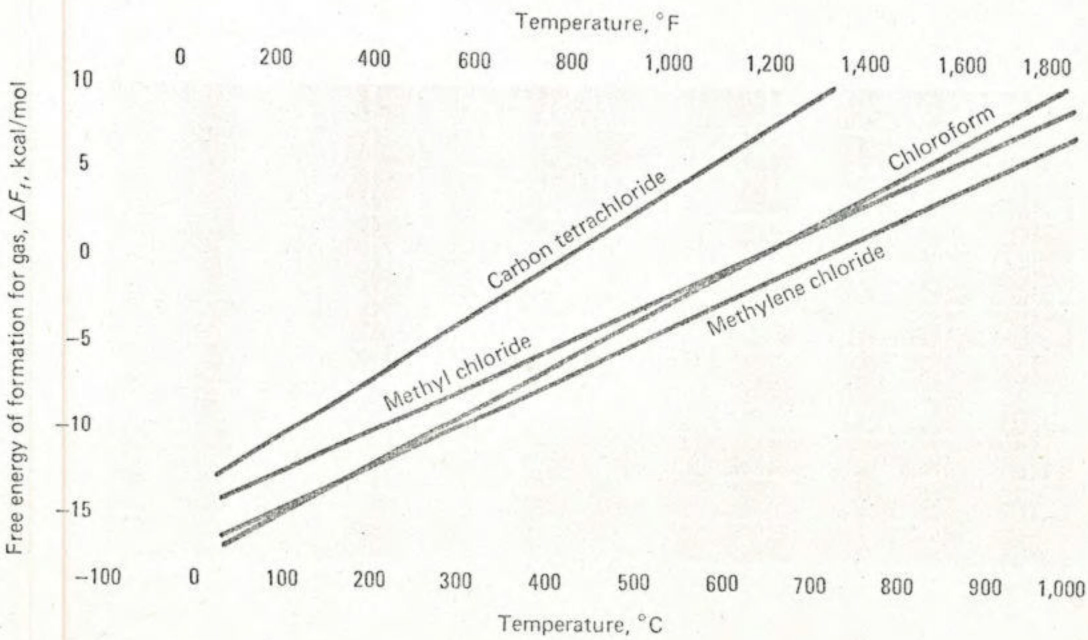


Heat of formation for gas — Fig. 11

Fig. 21-11	Temperature range, °C 0-500	500-1,000	Reference
Methyl chloride	☑	☑	7,15,418,727
Methylene chloride	☑	☑	7,15,418,727
Chloroform	☑	☑	15,418,727
Carbon tetrachloride	☑	☑	15,418,727

Free energy of formation for gas — Fig. 12

Fig. 21-12	Temperature range, °C 0-500	500-1,000	Reference
Methyl chloride	☑	☑	7,15,418,727
Methylene chloride	☑	☑	7,15,418,727
Chloroform	☑	☑	15,418,727
Carbon tetrachloride	☑	☑	15,418,727



of Zwolinski et al. [727] were chosen. Data from the different sources agree closely, with average deviations of only 0.4, 1.45, 0.4 and 0.3% for methyl chloride, methylene chloride, chloroform and carbon tetrachloride.

Liquid heat capacities for each chloromethane were extrapolated with the density-heat capacity relationship (Eq. 1—3, $n = 1$). Average deviations of extrapolated values from the data were 4.6, 3.6, 2.5 and 1.8% for the four chloromethanes.

Density—Fig. 21—5

Liquid densities for the chloromethanes were correlated with the modified Rackett equation (Eq. 15—1). Deviations between calculated and experimental values were small—less than 1%.

Surface Tension—Fig. 21—6

Surface tension data were augmented with the Othmer relation (Eq. 15—2, $n = 1.23$, 1.23, 1.17 and 1.22 for methyl chloride, methylene chloride, chloroform and carbon tetrachloride). Calculated values deviated from experimental ones on the average by less than 1%.

Viscosity—Fig. 21—7, 21—8

The results of Touloukian et al. [703], Landbolt-Bornstein [637] and Golubev [467] were the primary data sources for gas-phase viscosities at low pressure. At high temperatures, a modified Stiel and Thodos equation (Eq. 19—2) was adopted. Deviations between calculated and experimental values were 1.4, 0.6, 1.2 and 1.3% for methyl chloride, methylene chloride, chloroform and carbon tetrachloride.

The Guzman-Andrade relation (Eq. 1—6) was used to supplement experimental liquid viscosities. Deviations between correlated values and experimental ones averaged less than 2.5%.

Thermal Conductivity—Fig. 21—9, 21—10

Gas-phase thermal conductivities at low pressures were correlated with the Misic and Thodos equation (Eq. 10—2). The correlated results agreed with experimental data. Average deviations were 2.7, 5.8, 3.9 and 4.5% for methyl chloride, methylene chloride, chloroform and carbon tetrachloride.

The investigations of Touloukian et al. [19] and Landbolt-Bornstein [637] were primary sources for liquid thermal conductivities. The data were extended with a modified Stiel and Thodos equation (Eq. 10—3) to cover the entire saturated-liquid phase. Correlated values agreed well with the available data. Average deviations from the experimental data points were 2% or less for the four chloromethanes.

Heat and Free Energy of Formation—Fig. 21—11, 21—12

The findings of Rodgers et al. [727] were consulted for the heats and free energies of formation of the ideal gases. Results from the various contributors are consistent, with deviations of 1 kcal/mol or less in most cases.

The author

Carl L. Yaws is Associate Professor in the Chemical Engineering Dept. of Lamar University (P.O. Box 10053, Beaumont TX 77710). His industrial experience has been primarily in research-and-development and design with Exxon Corp., Ethyl Corp. and Texas Instruments Co.

He received a B.S. degree in chemical engineering from Texas A & I University, and M.S. and Ph.D. degrees in chemical engineering from the University of Houston, and has written more than 25 technical papers and articles on mass transfer, distillation, reaction kinetics, process scaleup and property data.

References

References 1 through 704 are listed in Parts 1 through 20 of this series.

705. Benning, A. F., and Markwood, W. H., Jr., *Ref. Eng.*, Vol. 38, Apr. 1939, p. 243.
706. Boltz, R. E., and Tuve, G. L., eds., "CRC Handbook of Tables For Applied Engineering Science," 2nd ed., CRC Press, Chemical Rubber Co., Cleveland, Ohio, 1973.
707. Challoner, A. R., and Powell, R. W., *Proc. Roy. Soc. London (Series A)*, Vol. 238, Jan. 1957, p. 90.
708. "Chloromethanes," Technical and Engineering Service Bulletin No. 21, Allied Chemical Corp., Industrial Chemicals Div., Morristown, N.J., 1966.
709. Denny, V. E., and Ferenbaugh, R., *J. Chem. Eng. Data*, Vol. 12, No. 3, 1967, p. 397.
710. Grolier, J. P. E., and Benson, G. C., *J. Chem. Eng. Data*, Vol. 20, No. 3, 1975, p. 243.
711. Hsu, C. C., and McKetta, J. J., *A.I.Ch.E. J.*, Vol. 9, No. 6, 1963, p. 794.
712. Hsu, C. C., and McKetta, J. J., *J. Chem. Eng. Data*, Vol. 9, No. 1, 1964, p. 45.
713. Katti, P. K., others, *J. Chem. Eng. Data*, Vol. 11, No. 4, 1966, p. 593.
714. Kobe, K. A., and Long, E. G., *Pet. Refiner*, Vol. 29, No. 3, Mar. 1950, p. 157.
715. Lapidus, I. L., others, "Thermophysical Properties of Matter," No. 1, ed. by V. A. Robinovich, U.S. Dept. Commerce, Springfield, Va., 1970, p. 102.
716. Linakis, K. N., and Bowrey, R. G., *Australian Chem. Eng.*, Vol. 14, No. 11, 1973, p. 3.
717. McGovern, E. W., *Ind. Eng. Chem.*, Vol. 35, 1943, p. 1230.
718. Mellan, I., "Source Book of Industrial Solvents," Vol. 2, Reinhold Publishing Corp., New York, 1957.
719. Kueller, C. R., and Ignatowski, A. J., *J. Chem. Phy.*, Vol. 32, No. 5, 1960, p. 1430.
720. Prydz, R., and Straty, G. C., Natl. Bureau of Standards Technical Note 392 (Revised), U.S. Govt. Print. Office, Washington, D.C., Sept. 1973.
721. Riddick, J. A., and Bunger, W. B., "Organic Solvents," Vol. 2, 3rd ed., Wiley-Interscience, New York, 1970.
722. Seshadri, D. N., others, *J. Chem. Eng. Data*, Vol. 14, No. 3, 1969, p. 322.
723. Sperry, E. H., and Mack, E., Jr., *J. Am. Chem. Soc.*, Vol. 54, 1932, p. 904.
724. Vitagliano, V., others, *J. Chem. Eng. Data*, Vol. 18, No. 4, 1973, p. 370.
725. Tanner, H. G., others, *Ind. Eng. Chem.*, Vol. 31, No. 7, 1939, p. 878.
726. Wettaw, J. F., others, *J. Chem. Eng. Data*, Vol. 14, No. 2, 1969, p. 181.
727. Zwolinski, B. J., others, *J. Phys. Chem. Ref. Data*, Vol. 3, No. 1, 1974, p. 117.
728. Horvath, A. L., *Chem. Eng.*, Vol. 83, No. 7, Mar. 29, 1976, p. 121.
729. Seshadri, D. N., others, *J. Indian Inst. Sci.*, Vol. 49, 1967, p. 117.
730. Seshadri, D. N., others, *J. Indian Inst. Sci.*, Vol. 50, 1968, p. 179.
731. Seshadri, D. N., others, *J. Indian Inst. Sci.*, Vol. 48, 1966, p. 65.
732. Griffing, V., others, *J. Phys. Chem.* Vol. 58, 1954, p. 1054.
733. Morgan, S. O., and Lowry, H. H., *J. Phy. Chem.*, Vol. 34, 1930, p. 2385.
734. Smyth, C. P., and Morgan, S. O., *J. Am. Chem. Soc.*, Vol. 50, 1928, p. 1547.