

Vapor Pressures and Boiling Points of Selected Halomethanes

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This critical review is a study of the vapor pressure—boiling point data from the triple point to the critical point for $\text{CH}_4\text{-}a\text{X}_a$ ($X = \text{Br}, \text{I}$) and $\text{CH}_4\text{-}(a+b+c+d)\text{F}_a\text{Cl}_b\text{Br}_c\text{I}_d$ halomethanes. The available data are carefully analyzed and the "best" data selected. The selection procedure is discussed. Uncertainties in the selected temperatures and pressures are reported. The selected data were fitted to the Antoine equation for data up to 1500 mm Hg pressure and the Wagner equation for data up to the critical point. Antoine constants for nineteen compounds and the Wagner constants for five compounds are reported. The enthalpy of vaporization at 298.15 K and at the normal boiling point have been computed.

Key words: Antoine equation; enthalpy of vaporization; halomethanes; vapor pressure—boiling point data; Wagner equation.

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1. Introduction

1.1. Scope and Objectives

As part of our work on the physical and thermodynamic properties of the haloalkanes (F, Cl, Br, I substituted), the vapor pressure—boiling point data from the triple point to the critical point of the $\text{CH}_4\text{-}X_a$ ($X=\text{Br}, \text{I}$) and $\text{CH}_4\text{-}(a+b+c+d)$ $\text{F}_a\text{Cl}_b\text{Br}_c\text{I}_d$ halomethanes have been compiled, critically evaluated, and selected. For convenience, two pressure regions are defined: the "low pressure region" covering the range from the triple point pressure to about $200 \text{ kN}\cdot\text{m}^{-2}$ (1500 mm Hg) pressure, and the "liquid-vapor coexistence region" covering the range from the triple point pressure to the critical point. The literature survey covered the period 1908 up to December 1976. Out of a total of sixty-nine of these halomethanes, low-pressure data are available for nineteen compounds, and high pressure data for five compounds. For several compounds only the boiling points at 760 mm Hg pressure (henceforth referred to as nbp) are available. The status of the vapor pressure—boiling point data of these halomethanes is reported in figure 1; it brings out clearly the gaps in "good" data.

The work on CH_3F , CH_2F_2 , CHF_3 , CF_4 , CH_3Cl , CH_2Cl_2 , CHCl_3 , CCl_4 has already been completed by the Thermodynamics Research Center (henceforth referred to as TRC)[1].¹

An extensive literature survey was carried out through Chemical Abstracts. Most of the compiled data were taken from the original articles, but in some cases the data were taken from abstracts because of the nonavailability of the original articles. In very few cases information on sample purity, method and accuracy of measurements was available. Also, in most cases, the temperature scale used was not defined. Certain authors reported the vapor pressure equation fitted to their experimental data but not the actual data.

1.2. Temperature Scale

The experimental temperature values were corrected to the International Practical Temperature Scale of 1968, IPTS—1968 [2] using the TRC Library Program [3] and are reported in this article.

The present work was carried out using the pressure units of the majority of the original papers, mm Hg or atmospheres,

¹ Figures in brackets indicate literature references.

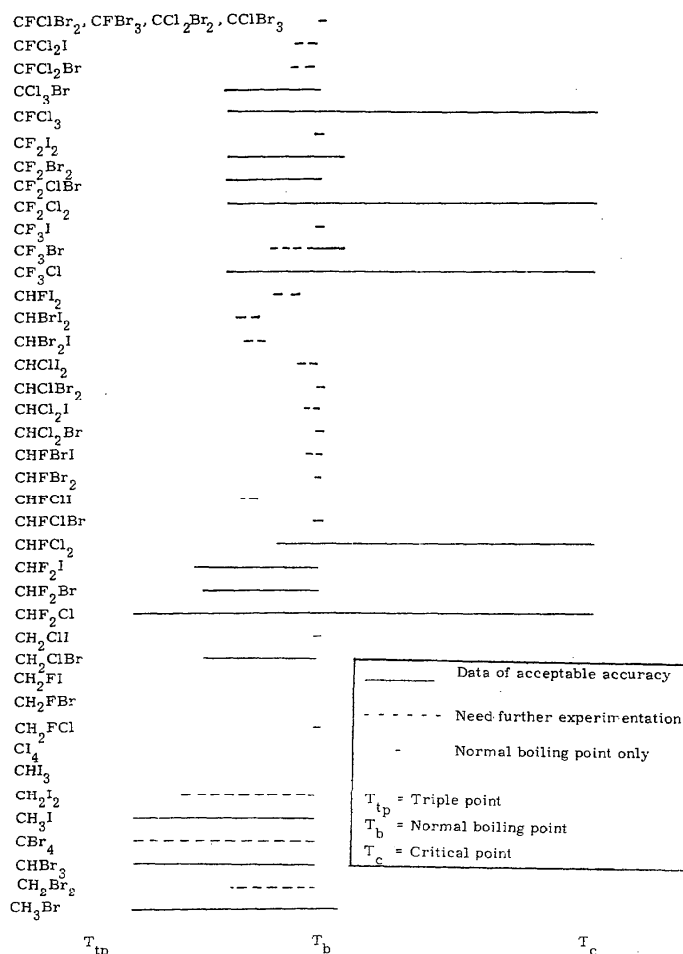


FIGURE 1. Status of the vapor pressure data for the halomethanes.

and the temperature unit, °C or K. The final results are presented in SI units. The following conversion factors were used.

$$\begin{aligned} 1 \text{ atm} &= 760 \text{ mm Hg} = 1.01325 \text{ bar} = 101.325 \text{ kN m}^{-2} \\ 1 \text{ lb in}^{-2} &= 51.71493 \text{ mm Hg} \\ 1 \text{ torr} &= 1 \text{ mm Hg} \\ 0 \text{ }^\circ\text{C} &= 273.15 \text{ K} \\ \text{ }^\circ\text{R} &= 1.8 \text{ K} \\ 1 \text{ kcal mol}^{-1} &= 4.184 \text{ kJ mol}^{-1} \end{aligned}$$

1.3. Evaluation and Selection Procedure

The information on sample purity, method and accuracy of measurements was adequate for very few compounds to permit proper assessment and selection. Only the experimental data were analyzed for selection and regression.

In analyzing the data, the work of each investigator was carefully scrutinized to ascertain the precision and accuracy of the actual measurements of pressure and temperature. Our judgement of "good" and "bad" data was based on the following criteria:

- (i) Source, method of purification, and purity of sample.
- (ii) Method of measurement and calibration of the measuring instruments.
- (iii) Accuracy of temperature and pressure measurements.
- (iv) Reproducibility of results.
- (v) Purpose of measurement.
- (vi) Number and closeness of data points.
- (viii) Range of investigated temperature and pressure.

Based on the above criteria, the available normal boiling point (nbp) values were analyzed and the "best" values were first selected.

The vapor pressure-boiling point data were then scrutinized and the "best" data were selected using the above selection criteria. In some cases these data were plotted as $\log P$ vs $1/T$ to check gross inconsistencies among the data of different investigators. In some cases there was no difficulty in identifying the "best" values; for example, those of Michels, or Messerly and Aston, and the nbp values of Timmermans and of Dreisbach and Martin. Further selection involved fitting the data to the vapor pressure equations. For this purpose two vapor pressure equations were selected. The Antoine equation, eq 1, is very simple and accurate over a limited range, i.e., from the triple point to about 1500 mm Hg pressure [4]. The Wagner equation [5] has been used to represent the vapor pressure data of argon, water, nitrogen, ammonia, and oxygen [6,7,7a] adequately from the triple point to the critical point. In this work the following form of the Wagner equation, eq 2, was used.

$$\log_{10} P(\text{mm Hg}) = A - B/[C + t(^{\circ}\text{C})] \quad (1)$$

$$\ln P_r = A[(1 - T_r)/T_r] + B[(1 - T_r)^{1.5}/T_r] + C[(1 - T_r)^3/T_r] + D[(1 - T_r)^7/T_r] + E[(1 - T_r)^9/T_r] \quad (2)$$

$T_r = T/T_c$; T_c is the critical temperature, K, and T is in K.

The set of regression constants obtained for a compound is a function of the regression program used. We have used the regression program from the TRC Library [3] which is a general weighted least squares regression program. The Antoine equation is converted into a form which is linear in the parameters, $t \log P = (AC - B) + At - C \log P$. The program calculates the weight factors in $t \log P$ and in $\ln P_r$ in eq 2, based upon the uncertainty in P or in t . We have used the uncertainty in T because it was readily available for many substances. Matrix inversion was carried out by the APLSV program.

The critical constants required for these regressions were taken from Kudchadker et al. [8] and are given in table 1. The average and maximum deviations tolerable in the regressions were fixed depending upon the accuracy of the experimental data. The final selected vapor pressure values in the form of an equation were assigned an uncertainty based upon the "maximum" error in the final regression. These deviations are defined in the following manner:

$$\text{Absolute average deviation} = \frac{\sum_{i=1}^N (P_{\text{obs}} - P_{\text{calc}})}{N} \quad (3)$$

$$\text{Standard deviation} = \left[\frac{\sum_{i=1}^N W_i (P_{\text{obs}} - P_{\text{calc}})^2}{N} \right]^{1/2} \quad (4)$$

where W_i is the normalized weight factor for the i th point and N is the number of data points. Once the absolute average deviation and standard deviation were established under the defined tolerance limits, further reliability of our selection and regression was checked by the following computations.

1. The derived Antoine constants were used to compute the normal boiling point (nbp) of each compound and compared with our selected value. The selected nbp value was used in the regression.

2. Computation of the enthalpy of vaporization, ΔH_v at 298.15 K and at the normal boiling point for each compound. For this purpose, the Clausius-Clapeyron equation, eq (5) was used.

TABLE 1. Critical constants of some halomethanes

Compound	T_c , K	$P_c \times 10^{-2}$, kN m ⁻²
CHF ₂ Cl	369.2	49.77
CHFCl ₂	451.58	51.8
CF ₃ Cl	302.0	38.70
CF ₂ Cl ₂	384.95	41.36
CFCl ₃	471.2	44.1

$$\Delta H_v = T(v_g - v_l)(dP/dT) \triangleq Z_g RT^2 (d \ln P/dT), \quad (5)$$

where v_g = vapor volume, v_l = liquid volume, and assuming $v_g \gg v_l$. The derivative, $d \ln P/dT$, was calculated using the Antoine or the Wagner equation. The vapor compression factor Z_g was calculated using the following relationship.

$$Z_g = P v_g / RT = 1 + B_v P / RT \quad (6)$$

Here B_v is the second virial coefficient. The experimental B_v values were fitted to the following model:

$$B_v = \sum_{i=0}^5 A_i T^{-i} \quad (7)$$

The calculated ΔH_v values were compared with the calorimetric values which gave a good indication of the fit of the vapor pressure equations to the experimental data. In the absence of the experimental B_v values, the ideal ΔH_v values, ΔH_v^0 , are reported assuming $Z_g = 1$.

The regression results for each compound using eq 1 and eq 2 are reported in tables 2 and 4, respectively. The following data are tabulated: i. The number of experimental data points used in regressing the vapor pressure equations. ii.

The lower and the upper pressure and temperature limits of the experimental data. iii. The computed vapor pressure equation constants. iv. The assigned uncertainty in the calculated temperature and pressure using the vapor pressure equation constants.

Tables 3 and 5 report the derived quantities using eqs 1 and 2, respectively. The tables contain the normal boiling point (nbp), dP/dT , ΔH_v at 298.15 K and at nbp, and the uncertainty in the calculated ΔH_v values.

Tables 6 and 7 give a comparison of our data with the literature values for selected halomethanes.

The data in the tables are reported in SI units.

The Antoine constants in table 2 are reported in pressure units of kN m^{-2} and are related to those reported in the text as follows: $A(\text{kN M}^{-2}) = A(\text{mm Hg}) - \log(7.500616)$; B and C remain the same

TABLE 2. Antoine constants, the upper and lower limits, and the uncertainties in calculated temperature and pressure

Compound	Number of data points	Lower limits		Upper limits		Antoine constants ^a			Uncertainty in calculated	
		t , °C	P , kN m^{-2}	t , °C	P , kN m^{-2}	A	B	C	t , °C	P , kN m^{-2}
CH ₃ Br	13	-70	1.7	5	105.5	6.21313	1044.42	244.684	±0.05	±0.07
CH ₂ Br ₂	5	0	1.5	100	101.3	6.95444	1784.9	263.73	±0.5	±0.7
CHBr ₃	15	+47	2.5	139	77.1	6.15631	1511.50	214.959	±0.05	±0.05
CBr ₄	9	102	6.7	190	101.3	4.89693	873.533	112.604	±1.5	±1.3
CH ₃ I	13	-14	9.3	42	97.9	6.09731	1138.29	235.774	±0.02	±0.03
CH ₂ I ₂	20	+20	0.09	182	101.3	6.1910	1715.7	218.17	±1.5	±0.5
CH ₂ ClBr	6	16	12.4	68	101.3	5.53797	903.382	187.694	±0.2	±0.4
CHF ₂ Cl	6	-79	11.4	-37	122.3	6.06382	808.919	240.161	±0.01	±0.05
CHF ₂ Br	6	-79	2.6	-15	104.8	6.34015	1013.1	249.46	±0.2	±0.5
CHF ₂ I	7	-46	4.2	+14	74.2	6.2323	1170.9	254.84	±0.2	±0.5
CHFl ₂	6	+26	4.0	60	15.1	5.7440	1357.9	238.06	±0.4	±0.13
CF ₃ Cl	4	-128	13.9	-81	101.3	5.92806	663.370	250.537	±0.01	±0.03
CF ₃ Br	6	-108	4.0	-57	104.5	6.27870	869.048	261.243	±0.1	±0.07
CF ₂ Cl ₂	9	-101	1.1	+6	372.3	5.94591	839.622	242.861	±0.05	±0.13
CF ₂ ClBr	22	-95	0.3	10	168.1	5.97618	940.155	240.794	±0.01	±0.07
CF ₂ Br ₂	7	-26	12.2	24	104.3	6.27598	1180.54	253.675	±0.02	±0.07
CFCl ₃	7	-37	6.3	20	88.6	6.01886	1047.04	237.276	±0.02	±0.03
CCl ₃ Br	4	0	1.5	104	99.3	6.5444	1650.8	258.82	±0.5	±0.13

^a $\log_{10} P(\text{kN m}^{-2}) = A - B/(C + t(^{\circ}\text{C}))$.

1 $\text{kN m}^{-2} = 7.500616$ mm Hg.

TABLE 3. The normal boiling point, dP/dT , and the enthalpy of vaporization at 298.15 K and at the normal boiling point calculated using the Antoine equation

Compound	nbp ^a		dP/dT , kN m ⁻² K ⁻¹		ΔH_v^b , kcal mol ⁻¹			ΔH_v , kJ mol ⁻¹		
	° C	K	298.15 K	nbp	298.15 K	nbp	Uncertainty	298.15 K	nbp	Uncertainty
CH ₃ Br	3.55	276.70	7.241	3.954	5.56	5.760	±0.050	23.26	24.098	±0.200
CH ₂ Br ₂	96.95	276.70	3.2	0.29		8.6	±.5		36.0	±2.0
CHBr ₃	149.21	422.36	0.04352	2.660	10.68 ^c	9.30 ^c	±.10	44.67	38.92	±.40
CBr ₄	189.5	462.6	0.00253	2.220		9.37 ^c	±.10		39.22	±.40
CH ₃ I	42.43	315.58	2.081	3.432	6.685	6.534	±0.010	27.970	27.338	±.040
CH ₂ I ₂	182.	455.2	0.0115	2.488	11.80 ^c	10.16 ^c	±.10	49.38	42.49	±.40
CH ₂ FCI	-9.1	264.0								
CH ₂ FBr	+18.	291.0								
CH ₂ FI	53.	326.0								
CH ₂ ClBr	68.06	341.21	0.8979	3.222	8.12 ^c	7.36 ^c	±.10	34.0	30.8	±.40
CH ₂ ClI	109.	382.0								
CHF ₂ Cl	-40.83	232.32		4.749		4.837	±.010		20.238	±.040
CHF ₂ Br	-15.7	257.4	13.8	4.329	5.5 ^c	5.62 ^c	±.10	23.0	23.5	±.4
CHF ₂ I	+22.2	295.4	3.846	3.560	6.1 ^c	6.09 ^c	±.10	25.0	25.5	±.4
CHFCl ₂	8.90	282.05 ^d	6.242 ^d	3.964 ^d	5.79 ^d	6.01 ^d	±.05	24.23	25.15	±.20
CHFCI ₂	36.	309.								
CHFCII	35.	308. (at 150 mm Hg)								
CHFB ₂	64.0	337.0								
CHFB ₂ I	103.	376.								
CHCl ₂ Br	90.1	363.2								
CHCl ₂ I	131.	404.								
CHClBr ₂	120.	393.								
CHClI ₂	200.	473.								
CHBr ₂ I	101.	374. (at 50 mm Hg)								
CHBrI ₂	101.	374. (at 25 mm Hg)								
CHFI ₂	125.	398.	0.1727	2.40	7.98 ^c	7.47 ^c	±.10	33.4	31.3	±.4
CF ₃ Cl	-81.44	191.71		5.410		3.764	±.010		15.749	±.040
CF ₃ Br	-57.86	215.29		4.902		4.46 ^c	±.10		18.6	±.4
CF ₃ I	-22.	251.								
CF ₂ Cl ₂	-29.77	243.38		4.314		4.807	±.020		20.112	±.080
CF ₂ ClBr	-4.01	269.14	8.421	3.912	5.4 ^c	5.56 ^c	±.10	23.0	23.3	±.4
CF ₂ Br ₂	+22.78	295.93	3.836	3.604	6.18 ^c	6.19 ^c	±.10	25.9	25.9	±.4
CF ₂ I ₂	80.	353.								
CFCl ₃	23.63	296.78	3.728	3.589	5.98	5.99	±.10	25.0	25.1	±.4
CCl ₃ Br	104.9	378.	0.2524	2.918	8.3 ^c	8.2 ^c	±.10	35.0	34.0	±.4
CFCl ₂ Br	50.	323. (at 725 mm Hg)								
CFCl ₂ I	45.	318. (at 210 mm Hg)								
CFCI ₂ Br	80.	353.								
CFBr ₃	106.5	379.6								
CCl ₂ Br ₂	120.	393.								
CClBr ₃	160.	433.								

^a Normal boiling point at 1 atm (101.325 kN m⁻²).^b Calculated using the Antoine constants with the nonideality correction.^c Ideal ΔH_v ($Z_g = 1.0$).^d Calculated using Wagner equation.1 kcal mol⁻¹ = 4.184 kJ mol⁻¹.

TABLE 4. The Wagner constants and uncertainties in calculated temperature and pressure

Compound	No. of data points	Wagner constants ^a					Uncertainty in calculated	
		A	B	C	D	E	T, K	P, kN m ⁻² (percent)
CHF ₂ Cl	20	-7.02339	+1.30656	-2.82438	+8.29080	-42.9691	±0.04	0.40
CHFCl ₂	7	-6.81022	+0.861064	-1.02842	-78.0366	+255.042	±.08	.05
CF ₃ Cl	7	-6.68480	+1.00163	-1.83445	-5.88596	+4.01573	±.04	.05
CF ₂ Cl ₂	17	-6.97671	+1.58642	-2.59664	-4.01823	+2.70631	±.08	.04
CFCl ₃	14	-7.00266	+1.71673	-3.50524	+11.8186	-31.7712	±.03	.03

^a $\ln P_r = A[(1 - T_r)/T_r] + B[(1 - T_r)^{1.5}/T_r] + C[(1 - T_r)^3/T_r] + D[(1 - T_r)^7/T_r] + E[(1 - T_r)^9/T_r]$. $T_r = T/T_c$; T and T_c in K.

TABLE 5. Enthalpy of vaporization and dP/dT at 298.15 K calculated using the Wagner equation

Compound	dP/dT , kN m ⁻² K ⁻¹	ΔH_v			
		kcal mol ⁻¹	Uncertainty	kJ mol ⁻¹	Uncertainty
CHF ₂ Cl	28.14	3.97	±0.02	16.61	±0.08
CHFC1 ₂	6.243	5.79	±.02	24.23	±.08
CF ₃ Cl	78.77	2.89	±.02	12.09	±.08
CF ₂ Cl ₂	17.65	4.19	±.02	17.53	±.08
CFCl ₃	3.737	6.00	±.02	25.10	±.08

TABLE 6. Comparison of some derived properties calculated by the Antoine and Wagner equations

Compound	nbp, K		dP/dT , kN m ⁻² at nbp		ΔH_v , kJ mol ⁻¹ at nbp	
	Antoine	Wagner	Antoine	Wagner	Antoine	Wagner
CHF ₂ Cl	232.32	232.32	4.749	4.743	20.24	20.27
CHFC1 ₂		282.05		3.959		25.15
CF ₃ Cl	191.74	191.76	5.410	5.415	15.75	15.77
CF ₂ Cl ₂	243.38	243.36	4.313	4.313	20.11	20.09
CFCl ₃	296.78	296.78	3.589	3.598	25.06	25.10

For CFCl₃ ΔH_v , kJ mol⁻¹ at 298.15 K are 25.0 by Antoine and 25.1 by Wagner equations.

TABLE 7. Comparison of the normal boiling points of this work with the literature selected values

Compound	Normal boiling point, K				
	This work	ESD[102]	ASHRAE [103]	Matheson [104]	Vargaftik [105]
CH ₃ Br	276.70	276.72		276.71	
CH ₂ Br ₂	370.10	369.52			
CHBr ₃	422.36	422.13			
CH ₃ I	315.58	315.57			
CH ₂ ClBr	341.21	341.21			
CHF ₂ Cl	232.32	232.33	232.37	232.49	232.4
CHFC1 ₂	282.07	282.05		282.07	282.05
CF ₃ Cl	191.74	191.72	191.71	191.75	191.6
CF ₃ Br	215.29	215.42	215.40	215.35	
CF ₂ Cl ₂	243.38	243.33	243.37	243.36	243.4
CF ₂ ClBr	269.14	269.14			
CB ₂ Br ₂	295.93	295.92		297.05	
CFCl ₃	296.78	296.74	296.98	296.97	296.8
CCl ₃ Br	378.20	377.06			

2. Bromomethane (CH₃Br)

Hsia [9] reported experimental data on a fractionally distilled sample over the temperature range -75° to +20 °C by the following equation:

$$\log P(\text{mm Hg}) = 10.3344 - (1375.625/T(\text{K})) - 1.11078 \\ \log T(\text{K}) + 8.559 \times 10^{-4} T(\text{K}). \quad (8)$$

They reported the accuracy of pressure measurement as ±0.5%. Equation (8) yields nbp=3.18 °C.

Egan and Kemp [10] used a 99.9 mole % pure sample and measured data from 13 to 790 mm Hg pressure with an accuracy of ±0.05°C in temperature and 0.01 mm Hg in pressure.

Beersmans and Jungers [11] reported data from -70° to +3.6 °C (13 to 761 mm Hg).

The following nbp values are available (complete list of references is available in the TRC Tables [1]).

nbp, °C	Authors	Remarks
3.18.....	Hsia [9]	Calculated from Equation.
3.65±0.05	Williams, Mecker [12]	
3.45.....	Varshni, Mohan [13].....	
4.5.....	Iarovenko [14]	
3.56.....	Egan, Kemp [10]	Calculated from vapor pressure data.
3.56.....	TRC (selected, [1])	

The high pressure data are not available for this compound. Based upon the sample purity and the accuracy of the temperature (±0.05 °C) and pressure measurements, the data of Egan and Kemp have been selected. The regression results using the Antoine equation are given below.

	<i>t</i> , °C	<i>P</i> , mm Hg
Average deviation ²	±0.002	±0.14
Maximum deviation032	.57
Standard deviation005	.20

Antoine constants: *A* = 7.08823; *B* = 1044.42; *C* = 244.684
nbp = 3.55 °C

The literature *B_v* values from 244 to 380 K [15] were fitted to the following expression.

$$B_v (\text{cm}^3 \text{mol}^{-1}) = -0.25224 \times 10^4 + 0.30682 \times 10^7 T^{-1} - 0.15246 \times 10^{10} T^{-2} + 0.35948 \times 10^{12} T^{-3} - 0.41964 \times 10^{14} T^{-4} + 0.13913 \times 10^{16} T^{-5} \quad (9)$$

The following values were obtained using Equations 5, 9 and the above Antoine constants.

<i>T</i> , K	<i>B_v</i> , cm ³ mol ⁻¹	<i>Z_g</i>	<i>dP/dT</i> , mm Hg deg ⁻¹	ΔH_v , kcal mol ⁻¹
276.70	-680	0.970	29.66	5.76
298.15	-539	0.952	54.31	5.56

The calculated nbp value agrees very well with the TRC selected value. Calorimetric ΔH_v value of 5.72 kcal mol⁻¹ at 276.70 K from Egan and Kemp [10] is in good agreement with our value of 5.76 kcal mol⁻¹.

3. Dibromomethane (CH₂Br₂)

Rex [16] reported limited low pressure data from 0 to 30 °C (11.5 to 56.4 mm Hg) on a carefully purified sample.

² Absolute average deviation.

The following nbp values are available (complete list of references is available in the TRC Tables [1]).

nbp, °C	Authors	Remarks
98.2.....	Lecat [17].	
97.23.....	Gross, Saylor [18].	
96.95.....	Timmermans [19].	
98.05.....	Varshni, Mohan [13].	
97.0.....	Iarovenko [14].	
96.95.....	TRC selected [1].	

Timmermans' value of 96.95 °C for nbp is selected.

The vapor pressure data of Rex with an uncertainty of ±0.1 °C and the selected nbp value with an uncertainty of ±0.01 °C were regressed to the Antoine equation. The results are given below:

	<i>t</i> , °C	<i>P</i> , mm Hg
Average deviation	±0.04	±0.08
Maximum deviation1	.2
Standard deviation05	.11
Antoine constants: <i>A</i> = 7.82954; <i>B</i> = 1784.9; <i>C</i> = 263.73 nbp = 96.95 °C		

These regression constants are selected and recommended.

Experimental *B_v* values and ΔH_v values are not available for this compound. The ideal ΔH_v values are computed using eq 5 and the Antoine constants reported above.

4. Tribromomethane (CHBr₃)

The available nbp values are listed below (complete list of references is available in the TRC Tables [1]).

nbp, °C	Authors	Remarks
149.57.....	Timmermans, Martin [20].	
150.4.....	Morgan, Yager [21].	
149.9.....	Ivin, Dainton [22].	
149.20.....	Van der Werf et al. [23].	
149.37.....	Varshni, Mohan [13].	
151.2.....	Iarovenko [14].	
149.20.....	Boublik, Aim [24].....	Calculated from vapor pressure data.
149.57.....	TRC (selected [1]).	

The vapor pressure data are measured by Boublik and Aim [24] from 18 to 578 mm Hg pressure range. They use chemically purified samples having the following properties

	<i>n_D²⁰</i>	<i>d₄²⁰</i> , g cm ⁻³
Boublik, Aim	1.5988	2.8916
Literature [1]	1.5976	2.8909

Temperatures were measured to ± 0.001 °C by calibrated platinum resistance thermometer-Mueller bridge assembly and pressures were maintained constant to ± 0.05 mm Hg.

These are the only vapor pressure data available and are selected. Their calculated nbp value is considerably lower than Timmermans and other values except that of Van der Werf et al.

Boublik and Aim did not report their sample purity and if we assume that the literature n_D and d values are for the purest sample, their sample is probably better than 99.9 mole % pure. An impurity of this order is not expected to make a change of 0.37 °C in the nbp value.

Boublik and Aim data were selected and fitted to the Antoine equation with an uncertainty of ± 0.001 °C in T , and the results are given below:

	t , °C	P , mm Hg
Average deviation	± 0.025	± 0.14
Maximum deviation	0.045	0.38
Standard deviation	0.027	0.17
Antoine constants: $A = 7.03141$; $B = 1511.50$; $C = 214.959$		
nbp = 149.21 °C		

Experimental B_v and ΔH_v values are not available for this compound. Hence ideal ΔH_v values are computed using eq 5 and the Antoine constants.

5. Tetrabromomethane (CBr₄)

The nbp values available are as follows:

nbp, °C	Authors
189.5	Bolas, Groves [25].
190	Friend, Hargreaves [26].
189.89 ..	Hildebrand [27].
189.39 ..	Varshni, Mohan [13].
189.5	Iarovenko [14].
189.5	TRC (selected [1]).

Using the nbp values of Hildebrand, Varshni and Mohan, and Iarovenko, a mean value of 189.5 ± 0.3 °C is selected for nbp. This value is the same as that of TRC.

The vapor pressure data from 50 to 760 mm Hg are reported by Bolas and Groves [25]. CBr₄ was prepared by them by two methods, one from carbon disulfide and another from bromopicrin. The experimental data differed by about ± 0.5 °C on these two samples. Uncertainties in temperature and pressure are assigned as ± 0.5 °C and ± 1 mm Hg, respectively. These data are selected and regressed (nbp included) to the Antoine equation. Two data points (121.0 °C, 100 mm Hg; 175.0 °C, 558 mm Hg) gave errors of the order of 2 deg. and hence were discarded in further analysis. The (final) regression results are given as follows:

t , °C P , mm Hg

Average deviation	± 0.15	± 1.4
Maximum deviation3	3.5
Standard deviation2	1.0
Antoine constants: $A = 5.77203$; $B = 873.533$; $C = 112.604$		
nbp = 189.5 °C		

The experimental data do not appear to be of good quality. Until better data become available, these Antoine constants are recommended.

In the absence of the experimental B_v and ΔH_v values, ideal ΔH_v values are reported.

6. Iodomethane (CH₃I)

The following nbp values are available:

nbp, °C	Authors	Remarks
42.43	Thorpe, Rodger [28].	
42.34	Brown, Acree [29].	
42.3	Biltz, et al. [30].	
42.49	Timmermans, Delcourt [31].	
42.6	Smyth, McAlpine [32].	
42.6	Hansen [33].	
42.6	Morgan, Yager [21].	
42.4	Varshni, Mohan [13].	
42.46	Fahim, Moelwyn-Hughes [34] ..	From vapor pressure data.
42.43	Boublik, Aim [24]	Do.
42.42	TRC (selected [1]).	

A complete list of references is available in the TRC Tables [1]. We have selected nbp = 42.43 °C based upon Boublik, Aim data [24].

Beckman [35] reported vapor pressure data from 28° to 41.3 °C (428 to 734 mm Hg) on a sample dried in the absence of light over anhydrous CuSO₄ and distilled. The pressures were measured by a Hg manometer and the temperatures by a Beckman thermometer. The accuracy of the measurements was not reported.

Thompson and Linnett [36] used a purified sample and reported data from 0.1 to 34.4 °C (140 to 570 mm Hg). Pressures were measured by using a Bourdon gage as zero instrument against a mercury manometer.

Reh [16] reported the data from 0 to 30 °C (140 to 480 mm Hg), on a repeatedly distilled, carefully purified sample.

Beersman and Jungers [11] used a mercury manometer and reported the data from 0 to 42.8 °C (140 to 761 mm Hg), the temperature accuracy being ± 0.02 °C.

Fahim and Moelwyn-Hughes [34] used a sample carefully purified by shaking with KOH pellets, dried with Na₂SO₄, distilled from phosphoric oxide and stored in the dark over mercury. The data were reported from 10° to 60 °C (220 to 1300 mm Hg).

Kolosovsky and Alimow [37] reported the following vapor pressure equation but gave no other details:

$$\log_{10}P(\text{mm Hg}) = -911.1341 + \frac{22267.5}{T(\text{K})} + 372.124 \log_{10}T - 0.274175 T. \quad (10)$$

This equation yields $\text{nbp} = 42.42^\circ\text{C}$ in very good agreement with our selected value.

Boublik and Aim [24, 38] used a carefully purified sample and reported data from -13.8 to $+41.4^\circ\text{C}$. Temperatures were measured to ± 0.001 degree and pressures to ± 0.05 mm Hg.

The data of Boublik and Aim are selected based upon the accuracy of their measurements and regressed to the Antoine equation with an uncertainty of $\pm 0.001^\circ\text{C}$ in temperature. The deviations are given below.

	$t, ^\circ\text{C}$	$P, \text{mm Hg}$
Average deviation	± 0.004	± 0.09
Maximum deviation022	.17
Standard deviation009	.07
nbp = 42.43°C		
Antoine constants: $A = 6.97241$; $B = 1138.29$; $C = 235.774$		

The calculated nbp value of 42.43°C agrees well with the TRC selected value.

Literature B_v values from 322 to 383 K [15] were fitted to the following model:

$$B_v(\text{cm}^3 \text{mol}^{-1}) = 0.31581 \times 10^4 - 0.27720 \times 10^7 T^{-1} + 0.59642 \times 10^9 T^{-2} - 0.92189 \times 10^{11} T^{-3} + 0.61630 \times 10^{14} T^{-4} - 0.13436 \times 10^{17} T^{-5} \quad (11)$$

Using these results, the following values are computed:

T, K	$B_v, \text{cm}^3 \text{mol}^{-1}$	Z_g	$dP/dT, \text{mm Hg K}^{-1}$	$\Delta H_v, \text{kcal mol}^{-1}$	
				calc	calorimetric
298.15.....	-812	0.982	15.61	6.68	
	(extrapolated)				
315.58.....	-648	0.975	25.74	6.535	6.539 [39]
	(nbp) (extrapolated)				

Andrews [39] reported the calorimetric ΔH_v value of $6.539 \text{ kcal mol}^{-1}$ at 42.2°C . This is in excellent agreement with our calculated value of $6.535 \text{ kcal mol}^{-1}$ at 42.43°C .

7. Diiodomethane (CH_2I_2)

The following nbp values are available.

nbp, $^\circ\text{C}$	Authors	Remarks
180.5–183.5 ..	Bacher, Wagner [40].....	Purified.
182.7–183	Kohlrausch, Ypsilanti [41].	
182.1–182.9 ..	Kohlrausch, Ypsilanti [41].	
188.....	Morgan, Yager [21].	
180.....	O'Connell (selected value) [42].	
182.....	TRC (selected value [1]).	

It is extremely difficult to select a good value for nbp. Until better data become available, the TRC nbp value of 182°C is selected.

Gregory and Style [43] reported nineteen very low pressure points from 0.67 to 7.53 mm Hg on a carefully purified sample. Some scattered data points are available between 10 and 40 mm Hg (30, 40, 42, 44, 45, 46) but they do not seem to be reliable enough for selection.

There are virtually no good data for this compound from 10 to 760 mm Hg.

Assigning an uncertainty in temperature of $\pm 0.5^\circ\text{C}$ to the Gregory and Style data and $\pm 1.0^\circ\text{C}$ to the selected nbp value, these twenty points were regressed to the Antoine equation with the following regression results.

	$t, ^\circ\text{C}$	$P, \text{mm Hg}$
Average deviation	± 0.6	± 0.3
Maximum deviation	1.4	3.7
Standard deviation	0.7	0.8
nbp = 182°C		
Antoine constants: $A = 7.1661$; $B = 1715.7$; $C = 218.17$		

In the absence of the experimental B_v values, ideal ΔH_v values are reported.

8, 9. Triiodomethane (CHI_3) and Tetraiodomethane (CI_4)

Experimental vapor pressure data are not available for these compounds.

10. Fluorochloromethane (CH_2FCI)

The following experimental values are available for nbp.

nbp, $^\circ\text{C}$	Authors
-9.1 ± 0.1 ..	Henne [47].
-8.5	Haszeldine [48].
-9.1	Landolt-Bornstein (selected [49]).
-9.1	Phillips, Murphy [50].
-9.1 ± 0.5 ..	Selected [1976].

No vapor pressure data are available for this compound.

11. Fluorobromomethane (CH₂FBr)

Haszeldine [48] reported 17.5 °C for the nbp and this is the only value available. Hence a temperature of 18 ± 1 °C is recommended for the nbp.

12. Fluoroiodomethane (CH₂FI)

Van Arbel and Janetzky [51] reported 53.4 °C for the nbp and Haszeldine [48], 52 to 53 °C. No details are available. The selected nbp based on these data is 53 ± 1 °C.

13. Chlorobromomethane (CH₂ClBr)

The following vapor pressure data are available:

<i>t</i> , °C	<i>P</i> , mm Hg	Authors	Remarks
68-69 ...	760	Forbes, Anderson [52].	
66-67 ...	760	Henry [53].	
15.71	93.34	McDonald et al. [54]	99.93 mole percent pure.
24.05	141.07	McDonald et al. [54].	
44.70	335.52	Do.	
57.17	526.37	Do.	
66.31	719.65	Do.	
67.99	760	Do.	

McDonald et al.'s data were fitted to the Antoine equation assigning an uncertainty of ±0.1 °C in *t* with the following deviations:

	<i>t</i> , °C	<i>P</i> , mm Hg
Average deviation	±0.08	±1.1
Maximum deviation16	-3.0
Standard deviation04	.64

nbp = 68.06 °C

Antoine constants: *A* = 6.41307; *B* = 903.382; *C* = 187.694

The calculated ideal Δ*H*_v values are reported. No calorimetric Δ*H*_v values are available for comparison.

14. Chloroiodomethane (CH₂ClI)

The only nbp value available is 109 °C at 760 mm Hg by Forbes and Anderson [52], and is recommended with an uncertainty of ±1 °C.

15. Difluorochloromethane (CHF₂Cl)

The following nbp values are available:

nbp, °C	Authors	Remarks
-39.8	Booth, Bixby [55].	
-40.6 to		
-40.8	Henne [47]	Purified.
-40.8 ± 0.1	Benning, McHarness [56].	
-40.67 ±		
0.07	Neilson, David [57]	99.98 mole percent pure.
-40.78	ASHRAE (selected [58]).	
-40.8	Phillips, Murphy [50].	
-40.87	Kletskii [59]	Calculated from the vapor pressure data.

Neilson and David [57] used a high purity sample; however, their nbp value is higher than that of Benning and McHarness [56] and of Kletskii [59]. The latter author measured the vapor pressure-boiling point data from about 75 mm Hg to the critical point. The sample contained 99.85 mole % CHF₂Cl, 0.10 mole % CF₂Cl₂, 0.05 mole % CHF₃ and CO₂. Temperatures were measured by a 30-ohm platinum resistance thermometer accurate to ±0.005 to 0.010 °C. The error in pressure measurement was reported to be ±0.03% of the measured pressure. Kletskii's data represent very accurate measurements. He represented the data by the following equation over the entire range (from -78 °C to +98 °C (*t*_c)):

$$\log_{10}P(\text{bar}) = 20.26376 - \frac{1813.787}{T} - 0.0625612 T + 1.9380 \times 10^{-4} T^2 - 3.22475 \times 10^{-7} T^3 + 2.29043 \times 10^{-10} T^4 \quad (12)$$

Based upon the sample purity and the accuracy of measurements, Kletskii's data are selected. Six data points in the range 85 to 917 mm Hg were fitted to the Antoine equation resulting in the following deviations.

	<i>t</i> , °C	<i>P</i> , mm Hg
Average deviation	±0.004	±0.14
Maximum deviation012	.42
Standard deviation006	.20
nbp =	-40.83 °C	
Antoine constants: <i>A</i> =	6.93892; <i>B</i> =	808.919; <i>C</i> =
	240.161	

Booth and Swinehart [60] reported high pressure data from 9 atm to the critical point using a purified sample and a static method of measurement. The temperatures were measured to ± 0.1 °C. Benning and McHarness [56] measured six data points from 263 mm Hg to the critical point using a purified sample. Only two data points are below 3000 mm Hg.

Based upon the accuracy of their measurements, Kletskii's data are selected and regressed to the Wagner equation, eq 2. The deviations are given below.

Wagner

Average deviation in P , atm	0.003
Maximum deviation, atm	-.018
Standard deviation, atm005

The Wagner equation gives an excellent fit to the selected data.

ΔH_v value at nbp was calculated using the Antoine constants and at 298.15 K using the Wagner constants. The compression factors, Z_g , required for this purpose were calculated using eq 6 from the volumetric data provided by ASHRAE [58] in the absence of the experimental B_v values. The calculated values are given below along with the calorimetric value at 232.50 K reported by Neilson and David [57].

T , K	Z_g	dP/dT , mm Hg K ⁻¹	ΔH_v , kcal mol ⁻¹	
			calc	calorimetric
232.32 (nbp)	0.965	35.63	4.846	4.833 at 232.50 K [57]
298.15	0.834	211.05	3.972	

The agreement with the calorimetric value is very good.

16. Difluorobromomethane (CHF₂Br)

The following data are available:

t , °C	P , mm Hg	Authors
-14.5	760	Swarts [61].
-14.5	760	Henne [50].
-78.5	19.5	Davidson [62].
-59.7	75	Do.
-49.6	140	Do.
-29.5	407	Do.
-18.5	678.5	Do.
-14.8	786	Do.
-15.0	760	Haszeldine [63].

Davidson measured pressures to 0.5 mm Hg with a mercury manometer and a meter stick; temperatures were measured to 0.2 deg with a calibrated copper-constantan thermocouple.

Davidson's data were selected and fitted to the Antoine equation. The fit was satisfactory as shown below:

	t , °C	P , mm Hg
Average deviation	± 0.06	± 1.6
Maximum deviation15	4.5
Standard deviation08	1.1
nbp = -15.7 °C		
Antoine constants: $A = 7.21525$; $B = 1013.13$; $C = 249.46$		

The ideal ΔH_v values are reported in the absence of the experimental B_v values.

17. Difluoroiodomethane (CHF₂I)

The following data are available:

t , °C	P , mm Hg	Authors	Remarks
-46.2	31.3	Ruff et al. [64]	Static method, purified.
-27.3	91.3	Do.	
-11.2	200.0	Do.	
0.0	327.0	Do.	
4.9	394.0	Do.	
10.6	500.5	Do.	
13.7	556.5	Do.	
20.5	760	Haszeldine [63].	
22.0	760	Iarovenko [14].	

Ruff et al. used a static method and a purified sample for the measurements. Their data were selected and regressed to the Antoine equation with an assigned uncertainty of ± 0.5 °C in temperature.

	t , °C	P , mm Hg
Average deviation	± 0.10	± 1.6
Maximum deviation	-.21	3.9
Standard deviation13	2.3
nbp = 22.2 °C		
Antoine constants: $A = 7.1074$; $B = 1170.9$; $C = 254.84$		

The calculated nbp of 22.2 °C is within our assigned uncertainty of Iarovenko's value.

Experimental B_v values are not available. Hence ΔH_v (ideal) are reported.

18. Fluorodichloromethane (CHFCl₂)

Henne [47] used a purified sample and reported an nbp of 9.0 ± 0.1 °C. Benning and McHarness [56, 65] used a static method and a purified sample and reported an nbp of 8.92 °C and seven data points from 130 mm Hg to the critical point. These data covered only three low pressure points. ASHRAE [58] and Phillips and Murphy [50] reported nbp of 8.9 °C, which is also the value of Benning and McHarness.

As there are only three low pressure data points, the Antoine equation was not fitted to these data. The available seven data points were fitted to the Wagner equation with almost exact fit (seven data points and six constants) which yielded $nbp = 8.90$ °C.

The ΔH_v values using the Wagner constants and the literature B_v values [15] from 238 to 450 K represented by eq 13 are given below:

$$B_v (\text{cm}^3 \text{mol}^{-1}) = 0.29105 \times 10^4 - 0.329758 \times 10^7 T^{-1} + 0.107850 \times 10^{10} T^{-2} - 0.336103 \times 10^{11} T^{-3} - 0.475335 \times 10^{14} T^{-4} + 0.645119 \times 10^{16} T^{-5} \quad (13)$$

T, K	$dP/dT, \text{atm K}^{-1}$	Z_g	$\Delta H_v, \text{kcal mol}^{-1}$
282.05 (nbp)	0.0391	0.973	6.007
298.15	.0616	.959	5.789

Calorimetric ΔH_v values are not available for comparison.

19. Fluorochlorobromomethane (CHFClBr)

The following nbp values are available:

$t, \text{°C}$	Authors	Remarks
36.11–36.18 ..	Burry, Sturtevant [66].....	Purified.
36.5.....	Haszeldine [48].	
36.0–36.7	Hine et al. [67]	Purified.
36. \pm 1	Selected (1976).	

Very scanty vapor pressure data are available for the following compounds.

No.	Com- pound	$t, \text{°C}$	$P, \text{mm Hg}$	Authors
20	CHFCl ..	35	150	Haszeldine [48].
		35 \pm 1	150	Selected (1976).
21	CHFBr ₂ ..	64.9	757	Swarts [61].
		64.5	760	Haszeldine [48].
		64 \pm 1	760	Selected (1976).

No.	Com- pound	$t, \text{°C}$	$P, \text{mm Hg}$	Authors
22	CHFBr ₁ ..	35	70	Haszeldine [48].
		102.–104	760	Do.
		103 \pm 1	760	Selected (1976).
23	CHCl ₂ Br ..	90.1	760	Timmermans, Martin [20].
		91	760	Forbes, Anderson [52].
		90.1 \pm 0.2	760	Selected (1976).
24	CHCl ₂ I.....	40	30	Auger [68].
		131	760	Do.
		42.2	38	Hine, Dowell [69].
		131 \pm 1	760	Selected (1976).
25	CHClBr ₂ ..	120	760	Forbes, Anderson [52].
		120 \pm 1	760	Selected (1976).
26	CHCl ₂	88	30	Auger [68].
		200	760	Do.
		200 \pm 1	760	Selected (1976).
27	CHBr ₂ 1 ...	91	42	Auger [68].
		101.4 ...	50	Do.
28	CHBrI ₂ ...	101	25	Do

No experimental details are given for any of these compounds. Most of the values are reported as rounded numbers. Hence selection is difficult.

29. Fluorodiiodomethane (CHF₂I₂)

Vapor pressure data from 30 to 110 mm Hg are available from Ruff et al. [64]. They used a static method for their measurement but did not report purity of the sample. Their data do not appear to be of good accuracy. As these are the only data available, they are selected and fitted to the Antoine equation assigning an uncertainty of ± 0.5 °C in t . The deviations are given below:

	$t, \text{°C}$	$P, \text{mm Hg}$
Average deviation	± 0.2	± 0.4
Maximum deviation4	.8
Standard deviation08	.2

nbp = 125. °C

Antoine constants: $A = 6.6191$; $B = 1357.9$; $C = 238.06$

The ideal ΔH_v values are reported.

30. Trifluorochloromethane (CF₃Cl)

The following nbp values are reported.

nbp, °C	Authors	Remarks
-81.35	Fiske [70].	
-82.	Haszeldine [63].	
-80.12	Varshni, Mohan [13].	
-81.9	Miller, Smyth [71].	
-81.32	Croll, Scott [72].	
-81.41	Albright, Martin [73]	Calculated from vapor pressure data.
-81.41	Selected (1976).	

Croll and Scott did not provide any details. Albright and Martin used a 99.9 mole % pure sample for their vapor pressure measurements. Hence -81.41 ± 0.05 °C is selected for the nbp value.

For the vapor pressure, three data points in the region 13 to 976 mm Hg are available from Ruff and Keim [74] on a purified sample. Thornton et al. [75] used a tensiometric method to measure data from 104 to 757 mm Hg. Albright and Martin [73] used a 99.9 mole % pure sample and a static method and reported data from 25 mm Hg to the critical point with a temperature accuracy of ± 0.01 °C. Mollerup and Fredenslund [76] measured vapor pressures at two temperatures in a high pressure ebullioscopic cell on a 99.8 mole % pure sample (11.902 atm at 255 K and 29.593 atm at 290 K).

The best vapor pressure data available are of Albright and Martin; these are selected but only three data points are below 2000 mm Hg. Hence these were supplemented by Thornton's data. Uncertainties in t of ± 0.05 °C to Albright and Martin data and ± 0.5 °C to Thornton data were assigned. The nbp of -81.41 ± 0.05 °C was also used in the regression.

The regression results with the Antoine equation are as follows:

	t , °C	P , mm Hg
Average deviation	± 0.08	± 2.5
Maximum deviation35	14.5
Standard deviation02	0.87

These deviations were much larger than the experimental uncertainties. Removal of some of the "bad" data points from Thornton improved the results substantially. The deviations in the final regression are as follows:

	t , °C	P , mm Hg
Average deviation	± 0.03	± 0.64
Maximum deviation08	2.2
Standard deviation04	1.0
nbp = -81.44 °C		

Though the agreement with the calculated and selected nbp value is satisfactory, the deviations in pressure are considerably larger than the uncertainty in the experimental values of Albright and Martin. The two sets of data do not seem to be compatible with each other. For this reason, the low pressure values of Albright and Martin (three points only) and the selected nbp value were regressed to the Antoine equation with almost exact fit. The derived Antoine constants are given below:

Antoine constants: $A = 6.80316$; $B = 663.370$; $C = 250.537$
nbp = -81.41 °C

The B_v values from 233 to 533 K [15] were used to develop the following expression:

$$B_v (\text{cm}^3 \text{mol}^{-1}) = 0.9924 \times 10^2 + 0.12199 \times 10^6 T^{-1} - 0.24590 \times 10^9 T^{-2} + 0.11324 \times 10^{12} T^{-3} - 0.23548 \times 10^{14} T^{-4} + 0.17506 \times 10^{16} T^{-5} \quad (14)$$

T , K	B_v , cm ³ mol ⁻¹	Z_g	dP/dT , mm Hg deg ⁻¹	ΔH_v , kcal mol ⁻¹
191.74 (nbp)	-556	0.965	40.60	3.76
298.15	-222	0.715		

For the region up to the critical point, the data of Albright and Martin and two points of Mollerup and Fredenslund were selected. The deviations in the Wagner equation fit were larger than the experimental uncertainty in the Albright and Martin data. Hence in the final analysis, only the Albright and Martin data were selected and regressed to the Wagner equation with an exact fit. The nbp value from this regression was also found to be -81.42 °C.

The above B_v values, eq 14, and the Wagner constants resulted in the following derived quantities.

T , K	dP/dT , atm K ⁻¹	Z_g	ΔH_v , kcal mol ⁻¹
191.74 (nbp)	0.05340	0.965	3.76
298.15	0.8086	0.715	2.89

Calorimetric ΔH_v values are not available for this compound.

31. Trifluorobromomethane (CF₃Br)

The following data are available.

<i>t</i> , °C	<i>P</i> , mm Hg	Authors	Remarks
-57.8	760	Banks et al. [77].	
-108.3	30	Davidson [62].....	Temp.: ±0.2 °C.
-105.2	38Do	Pressure: ±0.5 mm Hg.
-80.8	201	Do.	
-78.9	245	Do.	
-58.70	760	Waterman [78]	
-58	760	Haszeldine [63]	
-67.2	760	Miller, Smythe [71].....	Purified sample.
-58.79	729.11	McDonald et al. [54].....	99.9 mole percent pure.
-58.39	743.19	Do.	
-57.27	783.67	Do.	
-57.81	760	ASHRAE (selected [58]).	

The McDonald et al. vapor pressure data are for a 99.9 mole % pure sample and are reported to a hundredth of a degree. Hence these are selected as the best available. Graphical interpolation of these data yielded -57.92 °C for nbp as compared to -57.81 °C of ASHRAE and -58.70 °C of Waterman.

The data of Davidson and of McDonald et al. were plotted to check if Davidson's data followed a smooth trend compared to the more accurate McDonald et al. data. From the plot, the point (-80.8, 201.) was suspect. For further scrutiny these data were regressed to the Antoine equation assigning uncertainties of ±0.2 °C to Davidson's values and ±0.05 °C to McDonald's values. The following deviations were obtained.

	<i>t</i> , °C	<i>P</i> , mm Hg
Average deviation	±0.06	±0.31
Maximum deviation	-0.15	0.61
Standard deviation03	.19

nbp = -57.86 °C

Antoine constants: *A* = 7.15380; *B* = 869.048; *C* = 261.243

No experimental *B_v* values are available. The ΔH_v value at nbp calculated using *B_v* value from TRC [1] was 4.2 kcal mol⁻¹. It is not possible to verify this value since no calorimetric ΔH_v values are available.

32. Trifluoroiodomethane (CF₃I)

The following nbp values are available:

nbp, °C	Authors
-22.	Haszeldine [48].
-22.5	Nodiff et al. [79].
-22.5	Iarovenko [14].
-22. ± 1	Selected (1976).

Vapor pressure data are not available for this compound.

33. Difluorodichloromethane (CF₂Cl₂)

Gilkey et al. [80] reported the data from 90 mm Hg up to the critical point, using a static method and a purified sample. The accuracy of measurement was 0.5% in temperature and pressure. They did not report the experimental data but gave the vapor pressure equation which represented their data well. The calculated nbp value was -29.8 °C. Kells et al. [81] used a static method and a purified sample and reported data from 500 mm Hg to the critical point with an accuracy of ±0.1 °C in temperature and ±0.5 mm Hg in pressure. McHarness et al. [82] also used the static method to measure data from 8 mm Hg to the critical point, reporting only three data points in the low pressure region. Michels et al. [83] used a 99.95 mole % pure sample and reported accurate high pressure data only. ASHRAE [58] selected an nbp of -29.78 °C.

For the low pressure range, the data of Kells and of McHarness were selected as the best available, based upon the purity of the sample and the accuracy of measurement. These were fitted to the Antoine equation and the following deviations were obtained:

	<i>t</i> , °C	<i>P</i> , mm Hg
Average deviation	±0.02	±0.50
Maximum deviation04	1.2
Standard deviation003	0.23

nbp = -29.77 °C

Antoine constants: *A* = 6.82101 *B* = 839.622; *C* = 242.861

The literature *B_v* values [15] from 255 to 480 K were fitted to the following equation:

$$B_v (\text{cm}^3 \text{mol}^{-1}) = 0.12139 \times 10^3 - 0.12536 \times 10^6 T^{-1} + 0.13695 \times 10^8 T^{-2} - 0.81101 \times 10^{10} T^{-3} - 0.93989 \times 10^{10} T^{-4} - 0.82915 \times 10^{14} T^{-5} \quad (15)$$

<i>T</i> , K	<i>B_v</i> , cm ³ mol ⁻¹	<i>Z_g</i>	<i>dP/dT</i> , mm Hg deg ⁻¹	ΔH_v , kcal mol ⁻¹	Calc.	Exptl.
243.38	-823	0.959	32.53	4.81	4.80	[84]
298.15	-487	0.872

The nbp and ΔH_v values agree very well with the literature values.

For the region up to the critical point, the data of Kells et al., McHarness et al., and Michels et al. were selected and fitted to the Wagner equation. The fit was far from satisfactory. Michel et al.'s data are probably the most accurate; hence these and the low pressure data regressed earlier were fitted to the above model. The improvement in fit was excellent. Hence this fit was selected and the deviations are given below:

	Wagner
Average deviation in <i>P</i> , atm	±0.009
Maximum deviation, atm08
Standard deviation, atm018

The following derived quantities were obtained with the Wagner equation.

T, K	Z _g	dP/dT, atm K ⁻¹	ΔH _v , kcal mol ⁻¹	
			calc	calorimetric
243.38 .. nbp)	0.959	0.04259	4.801	4.80 [84]
298.15 ..	0.872	0.1743	4.19	

The results are quite satisfactory.

34. Difluorochlorobromomethane (CF₂ClBr)

Ruh and Davies [85] reported nbp of -3.97 °C while Miller and Smyth [71] used a pure sample and reported nbp of -3.3 °C. The most accurate low pressure data are available from Glew [86], who used a 99.9 mole % pure sample and measured temperatures accurate to ±0.003 °C. No high pressure data are available for this compound.

The data of Glew were selected and fitted to the Antoine equation. One point (-5.071 °C, 701.64 mm Hg) gave large deviation (+0.94 °C) and was a suspect. Removal of this point gave excellent results as shown below:

	Regression	
	I (all points)	II (one "bad" point removed)
Average deviation in t, °C	±0.085	±0.006
Maximum deviation, °C	-0.938	.01
Standard deviation, °C	0.044	.02
Average deviation in P, mm Hg	±2.48	±.02
Maximum deviation, mm Hg	10	.61
Standard deviation, mm Hg	1.24	.05
nbp, °C	-3.96	-4.01

From the regression analysis, barring one point, the data appear to be of excellent accuracy. Regression II is therefore selected.

Antoine constants: A = 6.85128; B = 940.155; C = 240.794.

Experimental B_v values are not available and hence ideal ΔH_v values are reported.

35. Difluorodibromomethane (CF₂Br₂)

The following nbp values are reported:

t, °C	Authors
24.5	Swarts [61].
24.5	Rathsburg [87].
25.0	Haszeldine [48].
23.84	Miller, Smyth [71].
22.84	Desirant [88].
23.5	Birchall, Haszeldine [89].

There is a large variation in the nbp values and moreover no experimental details are reported to evaluate the values. Davidson [62] measured the vapor pressure data from 20 to 480 mm Hg (six points) with an accuracy of 0.2 °C in temperature and 0.5 mm Hg in pressure. McDonald et al. [54] used a 99.9 mole % pure sample and reported data from 90 to 780 mm Hg. The temperatures and pressures are reported to a hundredth of a degree and one millimeter, respectively.

On the basis of the purity of the sample, the data of McDonald et al. were selected and fitted to the Antoine equation with an assigned uncertainty of ±0.1 °C in temperature. Regression results are given below.

	t, °C	P, mm Hg
Average deviation	±0.008	±0.17
Maximum deviation016	.44
Standard deviation004	.09
nbp = 22.78 °C		
Antoine constants: A = 7.15108 B = 1180.54; C = 253.675		

The ideal ΔH_v values are reported in the absence of the experimental B_v values.

36. Difluorodiodomethane (CF₂I₂)

McAlpine and Sutcliffe [90] reported 80.5 °C for the nbp of a purified sample. This is the only value available, and 80 ±1 °C is selected for the nbp value.

37. Fluorotrichloromethane (CFCl₃)

Ruff and Keim [74] reported three data points from 22 to 600 mm Hg. Benning and McHarness [56] used a static method and a pure sample and reported nbp of 23.69 °C. Their later measurements by an isoteniscope [65] on a carefully purified sample up to the critical point gave an nbp of 23.76 °C. Osborne [91] reported accurate low pressure data on a sample containing an impurity of about 0.05 mole %. The measurements were made with a Henson cathetometer with a scale calibrated in terms of a standard glass decimeter from the U.S. National Bureau of Standards. The observed readings were corrected to the international mm of mercury. Corrections were made for the effect of temperature, gravity, and the pressure exerted by the column of gas in the calorimeter tube leading to the manometer. They represented their data by the following equation.

$$\log_{10}(P(\text{mm Hg})) = 18.54101 - (1841.72/T) - 3.82423 \log_{10} T; T \text{ in K} \quad (16)$$

Their calculated nbp = 296.82 K = 23.67 °C. Varshni and Mohan [13] reported an nbp of 23.9 °C. ASHRAE [58] selected an nbp of 23.71 °C. Pavlova [92] reported their experimental data from -50° to +50 °C in the form of a vapor pressure equation but did not give actual experimental values.

The low pressure data of Benning and McHarness and the data of Osborne were selected in the first analysis as the best values. The uncertainty in Osborne et al. data is estimated as follows: $t = \pm 0.01$ °C and $P = \pm 0.1$ mm Hg. Regression to the Antoine equation resulted in the deviations given below:

	$t, ^\circ\text{C}$	$P, \text{mm Hg}$
Average deviation	± 0.039	± 0.54
Maximum deviation091	-2.01
Standard deviation049	0.80

These deviations appear to be larger than the experimental uncertainty assigned to Osborne et al. data. Hence only the Osborne et al. data were regressed which yielded much improved results as shown below:

	$t, ^\circ\text{C}$	$P, \text{mm Hg}$
Average deviation	± 0.009	± 0.09
Maximum deviation023	-.24
Standard deviation013	.12

Hence this regression was selected. The nbp value and the Antoine constants are given below.

nbp = 23.63 °C

Antoine constants: $A = 6.89396$; $B = 1047.04$; $C = 237.276$

The literature B_v values from 405 to 478 K [15] were fitted to the following model.

$$B_v (\text{cm}^3 \text{mol}^{-1}) = 0.11533 \times 10^4 - 0.14173 \times 10^7 T^{-1} \\ + 0.55787 \times 10^9 T^{-2} - 0.48506 \times 10^{11} T^{-3} \\ - 0.43683 \times 10^{14} T^{-4} \\ + 0.95990 \times 10^{16} T^{-5} \quad (17)$$

Extrapolation of eq 17 to obtain B_v values at say 298.15 K (296.78 K (nbp)) is not desirable because the equation is valid from 400 to 500 K.

Osborne et al. reported the calorimetric ΔH_v of $6.025 \pm .006$ kcal mol⁻¹ at 290.40 K. The ideal ΔH_v value calculated from the Antoine constants is 6.231 kcal mol⁻¹ at 290.40 K. The non-ideality correction is estimated to be -212 cal mol⁻¹ at 290.40 K from reference [91]. With this correction, the ΔH_v at 290.40 K is 6.019 kcal mol⁻¹ in excellent agreement with the calorimetric value. Hence using the selected Antoine constants and the non-ideality correction of -212 cal mol⁻¹, the ΔH_v values at nbp (296.78 K) and at 298.15 K have been calculated and reported below:

T, K	$dP/dT, \text{mm Hg K}^{-1}$	$\Delta H_v^\circ, \text{kcal mol}^{-1}$	Non-ideality correction kcal mol^{-1}	$\Delta H_v, \text{kcal mol}^{-1}$
296.78 (nbp)	26.92	6.199	0.212	5.99
298.15	27.96	6.192	0.212	5.98

The high pressure data of Benning and McHarness along with the low pressure data used for the Antoine Equation yielded the following deviations by the Wagner equation.

	P, atm
Average deviation	± 0.005
Maximum deviation03
Standard deviation009

The results are satisfactory. ΔH_v values obtained with the Wagner constants are same as reported above.

42. Trichlorobromomethane (CCl₃Br)

The following nbp values are available.

nbp, °C	Authors	Remarks
104.3.....	Wouters [93]	
105.....	Lecomte et al. [94]	
103.4.....	Zakharin [95]	
103.95.....	Varshni, Mohan[13]	
103.....	Miller [96]	

No details are available regarding sample purity, etc., and hence the selection of nbp is not made.

The vapor pressure data (only four points) from 11 to 745 mm Hg are available from Davison and Sullivan [97]. The uncertainty in pressure was ± 1 mm Hg and the uncertainty in temperature was estimated to be ± 0.5 °C. These are the only vapor pressure data available and are selected. The deviations from the regression to the Antoine equation are given below:

	$t, ^\circ\text{C}$	$P, \text{mm Hg}$
Average deviation	± 0.1	± 0.2
Maximum deviation14	.25
Standard deviation1	± 0.2
nbp = 104.9 °C.....		
Antoine constants: $A = 7.4195$; $B = 1650.8$; $C = 258.83$		

In the absence of the experimental B_v values, ideal ΔH_v values are reported.

Very scanty vapor pressure and nbp data, reproduced here, are available for the following compounds:

No.	Compound	<i>t</i> °C	<i>P</i> , mm Hg	Authors
38	CFC ₂ Br	50.4	727	Miller et al. [98].
39	CFC ₂ I	44-46	210	Haszeldine [48].
		87-90	935	Miller [96].
40	CFCIBr ₂	79.5-80.5	760	Haszeldine [48].
		80. ± 1	760	Selected (1976).
41	CFBr ₃	107	760	Rathsburg [87].
		106.2	760	Banks et al. [99].
		106	760	Miller, Smyth [71].
		107.95	760	Desirant [88].
		106.27	760	Birchall, Haszeldine [89].
		132	760	Voughan, Smith [100].
		106.5 ± 0.5	760	Selected (1976).
43	CCl ₂ Br ₂	192.5	760	Maithe [101].
		135	760	Lecomte et al. [94].

No.	Compound	<i>t</i> °C	<i>P</i> , mm Hg	Authors
		119.76	760	Varshni, Mohan [13].
		120. ± 1	760	Selected (1976).
44	CCIBr ₃	160	760	Lecomte et al. [94].
		160.78	760	Varshni, Mohan [13].
		160. ± 0.5	760	Selected (1976).

45. Comparison

Table 6 shows a comparison of some derived properties calculated by the Antoine and Wagner equations at the overlapping temperature, the nbp. The agreement is very good.

The normal boiling points and vapor pressures at selected temperatures of this work are compared in tables 7 and 8 with the literature calculated values of Engineering Science Data [102], ASHRAE [103], Matheson [104], and Vargaftik [105]. The agreement is within 0.5% in pressure near the critical point improving considerably at lower pressures.

TABLE 8. Comparison of the calculated vapor pressure values at selected temperatures of this work with the literature values for five halomethanes

Temperature, K	This work	ESD [102]	ASHRAE [103]	Vargaftik [105]
CHF ₂ Cl: <i>P</i> × 10 ⁻² , kN m ⁻²				
200	0.166	0.167	0.168	0.167
250	2.169	2.169	2.179	2.164
300	10.97	10.96	10.96	10.97
350	34.40	34.40	34.41	34.41
360	41.81	41.80	41.50	41.83
<i>T_c</i> , K	369.2	369.30	369.2	369.
<i>P_c</i> , atm	49.77	49.80	49.77	49.86
CHFCl ₂ : <i>P</i> × 10 ⁻² , kN m ⁻²				
250	0.242	0.243		0.243
300	1.945	1.936		1.940
350	7.947	7.921		7.958
400	22.32	22.25		22.30
430	37.16	37.08		37.10
440	43.48	43.42		43.44
450	50.62	50.59		50.65
<i>T_c</i> , K	451.58	451.55		451.35
<i>P_c</i> , bar	51.8	51.79		51.81

TABLE 8. Comparison of the calculated vapor pressure values at selected temperatures of this work with the literature values for five halomethanes—Continued

Temperature, K	This work	ESD [102]	ASHRAE [103]	Vargaftik [105]
$\text{CF}_3\text{Cl}: P \times 10^{-2}, \text{kN m}^{-2}$				
150	0.0525	0.0525		
200	1.543	1.545	1.548	1.545
250	10.40	10.39	10.41	10.35
280	23.38	23.42	23.38	23.38
290	29.61	29.70	29.63	29.62
300	37.06	37.20	37.07	37.12
T_c , K	302.0	302.29	302.0	302.28
P_c , bar	38.70	38.60	38.7	38.5
$\text{CF}_2\text{Cl}_2: P \times 10^{-2}, \text{kN m}^{-2}$				
200	0.0997	0.1001	0.0997	
250	1.333	1.335	1.333	1.349
300	6.834	6.845	6.851	6.924
350	21.57	21.56	21.66	21.76
360	26.21	26.19	26.29	26.40
370	31.59	31.57	31.61	31.77
380	37.86	37.81	37.70	37.95
T_c , K	384.95	384.95	385.2	385.0
P_c , bar	41.36	41.25	41.1	41.32
$\text{CFCl}_3: P \times 10^{-2}, \text{kN m}^{-2}$				
250	0.134	0.134	0.134	0.134
300	1.135	1.136	1.126	1.135
350	4.870	4.880	4.810	4.877
400	14.07	14.05	13.99	14.15
450	32.23	32.21	32.37	
460	37.41	37.44	37.57	
470	43.30	43.39	43.38	
T_c , K	471.2	471.19	471.15	471.2
P_c , bar	44.1	44.15	44.2	

1 atm = 1.01325 bar = 101.325 kN m⁻².

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