THERMODYNAMIC PROPERTIES OF CHLOROFORM

By Seshadri, D. N., Viswanath, D. S. and Kuloor, N. R.
(Department of Chemical Engineering, Indian Institute of Science, Bangalore-12, India)

[Received: January 30, 1968]

Abstract

Thermodynamic properties of chloroform have been evaluated up to a temperature of 750°K and a pressure of 200 atmospheres, using Martin and Hou equation of state. Tables of thermodynamic properties and a temperature entropy diagram are presented.

Literature Survey

(1) *Molecular Weight and Critical Constants*:

The data on the critical constants of chloroform determined by various investigators are presented in Table-1.

Table 1

Molecular weight and critical constants of chloroform

Molecular weight of chloroform = 119.39

Year	Investigator	T_c, °K	P_c, atm.	d_c gm./c.c.	Method	Reference
1878	Sajotchewsky	533.16	54.9	......	a	20
1895	Pictet and Altschul	531.96	......	......	a	17
1902	Kuenen and Robson	535.06	53.8	......	a	12
1923	Herz and Neukirch	535.66	......	0.496	a, b	10
1934	Harand	536.66	......	......	a	9
1943	Fischer and Reichel	536.76	......	......	c	6
Values selected		536 71	54.0	0.50		

a = disappearance of the meniscus.

b = law of rectilinear diameter.

c = disappearance of the droplets after the meniscus has broadened.

In the above table, the data prior to 1900 are included for historical completeness only. Chloroform used by Kuenen and Robson[12] was prepared from chlorol and was carefully dried with calcium chloride.

Herz and Neukirch[10] have not stated the purity of chloroform used in their investigation. However,the accuracy of the temperature determinations is stated to be $\pm 0.2^\circ C$.

Though Harand[9], and Fischer and Reichel[6] did not state the purity of the sample, they have done careful work. The value for the critical temperature determined by Harand, and Fischer and Reichel agree very closely. Hence the values are averaged and this value has been used for the present investigation.

The critical pressure and density are not known to a great degree of accuracy. Hence the values were rounded off to two significant digits and were used for this work.

2. *Vapour Pressure*:

The vapour pressure of chloroform has been determined by various investigators like Beckmann and Liesche[1], Drucker *et al*[5], Herz and Rathmann[10], Scatchard and Raymonds[21], Kuenen and Robson[18], Rex[19]. and Schmidt[22, 23]. Stull[27] has made a critical compilation of the vapour pressure of chloroform up to the critical point. Data up to a temperature of 433°K are available in the International Critical Tables[33]. The available vapour pressure data along with the range of availability are presented in Table-2.

Kuenen and Robson[12] dried chloroform carefully with calcium chloride, but they were unable to reduce the action of chloroform on mercury (which takes place at high temperatures). They did not mention the accuracy of the vapour pressure data. Beckmann and Liesche[1] have not mentioned the method of preparation of chloroform and the accuracy of their vapour pressure determinations.

TABLE 2

Vapour pressure of chloroform

Year	Investigator	Range of temperature, °K	Range of pressure, atm.	Reference
1902	Kuenen and Robson	517.7 – 536 2	42 7 – 54 6	12
1912	Herz and Rathmann	300 2 – 334.2	0.29 – 1.0	11
1914	Beckmann and Liesche	291.2 – 343.2	0.2 – 1.4	1
1915	Drucker *et al.*	209.0 – 262 9	0.0 – 0.04	5
1916	Rex	273.2 – 303.2	0.08 – 0.32	19
1921	Schmidt	293.2 – 373 2	0.22 – 3.2	22
1926	Schmidt	273.2 – 303.2	0.08 – 3.2	23
1928	International Critical Tables	213.2 – 433.2	0.0 – 11.6	33
1938	Scatchard and Raymonds	308.2 – 333.2	0.3 – 0.96	21
1947	Stull	215.0 – 536.2	0.0 – 54	27

The vapour pressure data of chloroform determined by Drucker *et al*[5]. pertain to pressures up to 0.04 atm. Though the purity of the sample used is not reported, the errors in the pressure measurements are stated to be around 0.001 mm. However, as this work does not encompass such a low pressure, the data of Drucker *et al.* have not been used for this investigation.

Rex[19] used the Merck A. R. quality chloroform. The sample was carefully fractionated, then shaken with concentrated sulfuric acid, and finally with distilled water, and dried. The accuracy of the vapour pressure data is not presented.

Schmidt[22, 23] also did not state the purity of the chloroform used except to state that the sample was subjected to careful drying and fractional distillation. The accuracy of the data is not mentioned.

Scatchard and Raymonds[21] did not mention the purity of the sample used. The errors in the measurement of pressure are stated to be less than 0 05 mm.

For this investigation all the available vapour pressure data were combined and smoothened. The smoothened vapour pressure data have been used for this investigation.

The vapour pressure data over a temperature range of 275°K to 340°K, which covers a pressure range up to 1.2 atmospheres, were fitted by the method of least squares, to the equation :

$$\log P = A + B/T + C \log T + D T \qquad [1]$$

where $A = -29.593966$

$B = -1025.8492$

$C = 14.881037$

$D = -1.4702661 \times 10^{-2}$.

This equation was found to predict vapour pressures with average absolute and maximum deviations of 0.75% and 1.43% respectively.

The vapour pressure data over the temperature range of 340°K to the critical point which covers a range of pressure of 1.2 atmospheres to 54 atmospheres was fitted to the equation :

$$\log P = A_1 + B_1/T + C_1 \log T + D T \qquad [2]$$

where $A_1 = 14\ 0880803$

$B_1 = -1958.5807$

$C_1 = -3.3974131$

$D_1 = 1.06028811 \times 10^{-3}$

The average absolute and maximum deviations of vapour pressures evaluated using this equation are 0.58% and 1.52% respectively.

3. *Saturated Liquid and Vapour Densities*:

The density of saturated liquid has been determined by Morgan and Lowry[16], Schulze[24], Smyth and Morgan[25], Coop[3], Thorpe[28], and by Herz and Neukirch[10]. The range of available liquid densities of various investigators is presented in Table-3.

TABLE 3

Saturated liquid densities of chloroform

Year	Investigator	Range of temperature, °K	Reference
1880	Thorpe	273 – 334	28
1921	Schulze	278 – 299	24
1923	Herz and Neukirch	506 – 536	10
1928	Morgan and Lowry	213 – 333	16
1928	Smyth and Morgan	203 – 333	25
1937	Coop	193 – 293	3

Thorpe[28] determined the density of saturated liquid up to the boiling point. Though the accuracy of the data is not mentioned his data agree very closely with those of Smyth and Morgan and Morgan and Lowry, who claim their volumes to be determined with a precision of 1 part in 100,000.

Ramsay and Aston[18] have presented some data on the liquid density of chloroform. These values are stated to be those of Thorpe.

Coop[3] did not mention the purity of the sample and the accuracy of the data.

Liquid density at high temperatures have been determined by Herz and Neukirch[10]. The sample of chloroform used by these investigators was from Kahlbaum and was purified by drying over calcium chloride and carefully fractionated. The accuracy of the density data has not been mentioned.

Herz and Neukirch[10] have also determined saturated vapour densities of chloroform over a temperature range of 482 to 536°K.

The vapour densities over a temperature range of 285°K to 480°K were evaluated using Martin and Hou equation (Equation 5). For this investigation the saturated liquid densities of Thorpe, Herz and Neukirch, Morgan and Lowry and Smyth and Morgan, the vapour densities of Herz and Neukirch and the calculated vapour densities were combined and a smooth curve was drawn. The densities of saturated liquid wherever not available (over the temperature range of 330°K to 500°K) were evaluated from the smooth curve taking into consideration the observance of the law of rectilinear diameters.

(4) *Heat Capacity of the Saturated Liquid*:

The heat capacity of saturated liquid has been determined by Williams and Daniels[31] over a large of temperature of 295 – 319°K, by Dolezalek and Schulze[4] over a temperature range of 223 – 293°K and by Staveley *et al.*[26] over a temperature range of 284 – 329°K. The extent of purity of the samples used is not reported by these investigators. However Stavely *et al.*[26] claim their data to be accurate to ± 1%.

For this investigation the heat capacity data of all the investigators were combined, smoothened, and were used. The smoothened data agree with the actual values within 1%.

(5) *Heat of Vaporization*:

Latent heat of vaporization of chloroform has been experimentally determined by the calorimetric method over a range of temperature of 273 – 314°K by Fletcher and Tyrer[7]. The values are claimed to be accurate to within ± 0.1 cal/gm Heats of vaporization at the boiling point have also been determined by Marshall[13], Mathews[15], Writz[32] and by Tyrer[29] The data of Mathews[15] is in very good agreement with that of Fletcher and Tyrer[7]. The samples used by Mathews[15] were checked for purity against density and refractive index at 20°C and by determining the normal boiling point. The samples used by Tyrer[29] and Marshall[13] were fractionated and the purity of the sample was checked by the density and the boiling point The data of Fletcher and Tyrer[7] at the normal boiling point is about 1% higher than that of Tyrer and 2% higher than those of Marshall and Mathews. The smoothened data of all the investigators were used for this work.

Heat of vaporization calculated by Clausius-Clapeyron equation namely,

$$\Delta H_v = \frac{dP/dT}{T(V_g - V_1)} \qquad [3]$$

agrees with the smoothened data with maximum and average absolute deviations of 1.5% and 0.5% respectively.

Heat of vaporization above a temperature of 330°K was evaluated using the Clausius-Clapeyron equation.

(6) *Heat Capacity of the Ideal Gas*:

Heat capacity of ideal gas have been evaluated by Vold[30] up to a temperature of 500°K and by Gelles and Pitzer[8] up to a temperature of 1500°K. The data of Vold[30] are stated to be accurate to 97%. The data of Gelles and Pitzer[8] are more recent and extend to a large temperature range. Hence, the data of Gelles and Pitzer were used for this work. The data of Gelles and Pitzer were fitted by the method of least squares to the equation,

$$C_p^* = a + bT + cT^2 + dT^3 \qquad [4]$$

where $a = 7.1083$

$b = 3.6969 \times 10^{-2}$

$c = -2.9613 \times 10^{-5}$

$d = 8.4214 \times 10^{-9}$

over a temperature range of 250 – 1500°K.

Equation [4] fits the data with maximum and average absolute deviations of 1.1% and 0.43% respectively. For this work Equation [4] with the constants as given above is used.

CALCULATION OF THERMODYNAMIC PROPERTIES

For the calculation of thermodynamic properties Martin and Hou equation of state, namely,

$$P = \frac{RT}{(V - b_0)} + \frac{A_2 + B_2 T + C_2 \exp.\,(-KT/T_c)}{(V - b_0)^2} + \frac{A_3 + B_3 T + C_3 \exp\,(-KT/T_c)}{(V - b_0)^3} + \frac{A_4}{(V - b_0)^4} + \frac{B_5 T + C_5 \exp.\,(-KT/T_c)}{(V - b_0)^5} \quad [5]$$

with $K = 5.475$ has been used.

The constants evaluated by the method outlined by the authors[14] are:

$b_0 = 6.054802 \times 10^{-2}$

$A_2 = -21.5847159$

$B_2 = 1.31856963 \times 10^{-2}$

$C_2 = 30.306821$

$A_3 = 3.17370469$

$B_3 = -1.4828215 \times 10^{-3}$

$C_3 = -5.4014024$

$A_4 = -1.93684745 \times 10^{-1}$

$B_5 = 1.19430307 \times 10^{-5}$

In the range of available data Equation [5] was found to predict pressures with average absolute and maximum deviations of 1.37% and 2.70% respectively.

Specific volumes of saturated and superheated vapour were calculated using Equation [5] by making use of Newton-Raphson iterative method on an IBM 1620 digital computer, for various temperatures and pressures.

Entropy and Enthalpy of the Superheated Vapour :

Considering the entropy and enthalpy to be functions of volume and temperature, we have,

$$dS = (\partial S/\partial T)_V \, dT + (\partial S/\partial V)_T \, dV \quad [6]$$

Using Maxwell's relations, we obtain,

$$dS = (C_v^* /T)\, dT + (\partial P/\partial T)_V\, dV \qquad [7]$$

Using $dH = TdS + VdP$ in Equation [7] we obtain

$$\begin{aligned} dH &= C_v^*\, dT + T(\partial P/\partial T)_V\, dV + VdP \\ &= C_v^*\, dT + d(PV) - PdV + T(\partial P/\partial T)_V\, dV \end{aligned} \qquad [8]$$

From Equation [5] we have

$$(dP/dT)_V = \frac{R}{(V-b_0)} + \frac{B_2 - (K/T_c)\, C_2 \exp.\,(-KT/T_c)}{(V-b_0)^2}$$

$$+ \frac{B_3 - (K/T_c)\, C_3 \exp\,(-KT/T_c)}{(V-b_0)^3} + \frac{B_5 + C_5\,(K/T_c) \exp.\,(-KT/T_c)}{(V-b_0)^5} \qquad [9]$$

Using Equations [7] and [8],

$$S = \int (C_v^* /T)\, dT + \int (\partial P/\partial T)_V\, dV \qquad [10]$$

and

$$H = \int (C_v^*)\, dT + \int T(\partial P/\partial T)_V\, dV - \int PdV + PV \qquad [11]$$

Using Equations [4] and [9] in the above equations and carrying out the integration, we obtain expressions for entropy and enthalpy as :

$$S = (a-R)\, ln\, T + bT + (c/2)T^2 + (d/3)T^3 + R\, ln\,(V-b_0)$$

$$- \frac{B_2}{(V-b_0)} - \frac{B_3}{2\,(V-b_0)^2} - \frac{B_5}{4\,(V-b_0)^4}$$

$$+ \left[\frac{C_2}{(V-b_0)} + \frac{C_3}{2\,(V-b_0)^2} + \frac{C_5}{4\,(V-b_0)^4}\right] (K/T_c) \exp.\,(-KT/T_c) + C_S \qquad [12]$$

and

$$H = (a-R)\, T + (b/2)\, T^2 + (c/3)\, T^3 + (d/4)\, T^4$$

$$+ \frac{A_2 + (1 + KT/T_c)\, C_2 \exp.\,(-KT/T_c)}{(V-b_0)} + \frac{A_3 + (1 + KT/T_c)\, C_3 \exp.\,(-KT/T_c)}{(V-b_0)^4}$$

$$+ \frac{A_4}{3\,(V-b_0)^3} + \frac{(1 + KT/T_c)\, C_5 \exp.\,(-KT/T_c)}{4\,(V-b_0)^4} + PV - RT + C_H \qquad [13]$$

where C_S and C_H are the constants of integration.

Reference State :

The choice of the reference state depends on the convenience and the information available. The values of the constants of integration are dependent on the reference state chosen. Further, the reference state chosen should facilitate easy comparison and utilization of the tabulated data.

As has been pointed out by Canjar and Manning[2], the choice of the reference state as $H=0$ and $S+R \ln P=0$ for elements at absolute zero of temperature and at zero pressure would be applicable not only for pure substances but also for a mixture of pure sustances that undergo a chemical reaction. But it is necessary to have a knowledge of the heat of formation of the compound. In the present work as the heats of formation were available, the reference state $H=0$ and $S+R \ln P=0$ for elements at absolute zero of temperature and at zero pressure has been used.

Entropy value at the normal boiling point was evaluated using the ideal gas thermodynamic properties and the Berthelot correction. Enthalpy at the normal boiling point was evaluated by making use of the value of -22.8 K cal./mole for ΔH_0^0, the heat of formation at 0°K, the ideal gas thermodynamic properties and the Berthelot correction for enthalpy. The integration constants C_S and C_H were evaluated using the values of entropy and enthalpy at the normal boiling point. The values thus evaluated are:

$$C_S = 25.30 \text{ cal./mole } ^\circ\text{K}$$

$$C_H = -22915 \text{ cal./mole.}$$

Entropy and enthalpy of the superheated vapour were evaluated by making use of the calculated specific volume in Equation [1.] and [13].

Entropy and enthalpy of saturated vapour were evaluated by using the the experimental specific volumes in Equations [12] and [13]. Wherever the experimental data were not available these were calculated using Equation [5] and were used.

Entropy and Enthalpy of the Saturated Liquid :

The entropy of vaporization is related to the heat of vaporization by the relation

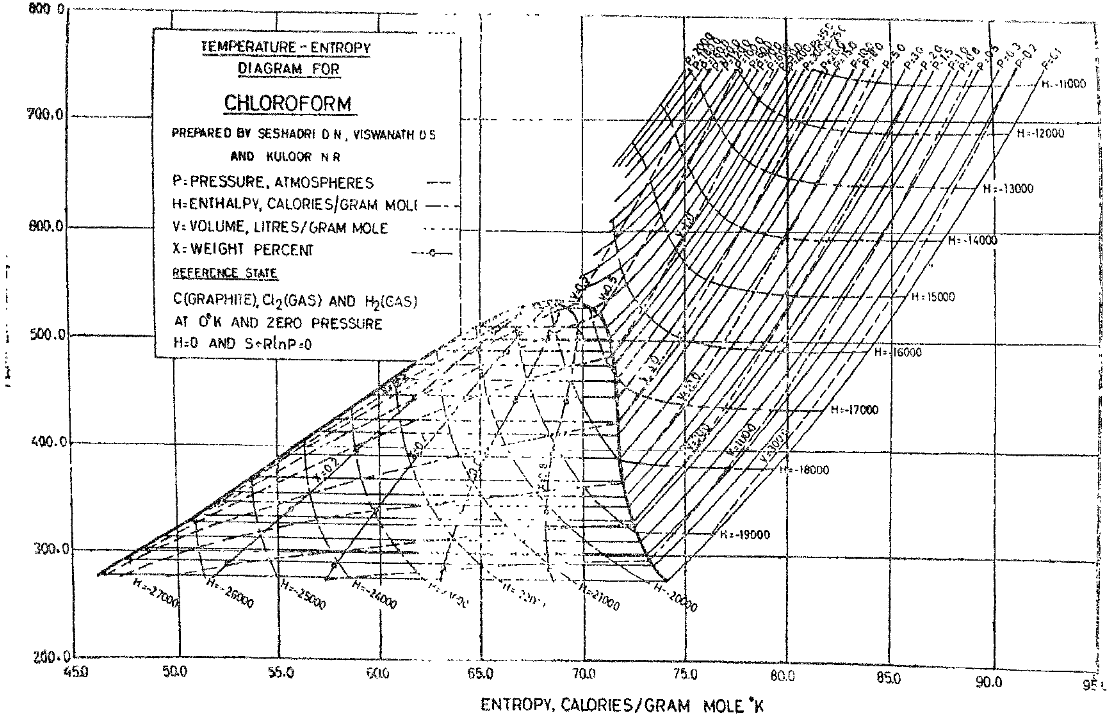
$$\Delta H_v = T \Delta S_v \qquad [14]$$

The entropy and enthalpy of the saturated liquid were calculated using the equations

$$S_l = S_g - \Delta S_v \qquad [15]$$

$$H_l = H_g - \Delta H_v \qquad [16]$$

The properties of saturated and superheated chloroform are presented in Tables 5 and 6 and in graphical form as Figure. 1.


TEMPERATURE - ENTROPY
DIAGRAM FOR
CHLOROFORM
PREPARED BY SESHADRI D N, VISWANATH D S
AND KULOOR N R
P: PRESSURE, ATMOSPHERES
H: ENTHALPY, CALORIES/GRAM MOLE
V: VOLUME, LITRES/GRAM MOLE
X: WEIGHT PERCENT
REFERENCE STATE
C(GRAPHITE), Cl2(GAS) AND H2(GAS)
AT 0°K AND ZERO PRESSURE
H=0 AND S+R ln P=0
ENTROPY, CALORIES/GRAM MOLE °K
45.0
50.0
55.0
60.0
65.0
70.0
75.0
80.0
85.0
90.0
200.0
300.0
400.0
500.0
700.0
H=-11000
H=-12000
H=-13000
H=-14000
H=-15000
H=-16000
H=-17000
H=-18000
H=-19000
H=-20000
H=-21000
H=-24000
H=-25000
H=-26000
H=-27000
P=5.0
P=3.0
P=2.0
P=1.5
P=0.3
P=0.2
V=0.5
V=1.0
V=10.0
V=200
V=1000
V=3000

INTERNAL CONSISTENCY OF THE TABULATED RESULTS

The relation $dH = TdS + VdP$ may be used to check the internal consistency of the entropy and enthalpy values.

At constant pressure,

$$dH = TdS \qquad [17]$$

Hence, $dH = d\,(TS) - SdT$ from which

$$H)_1^2 = T_2S_2 - T_1S_1 - \int_1^2 SdT \qquad [18]$$

Internal consistency checks were made for superheated region by using Equation [18]. The definite integral in Equation [18] was evaluated by Simpson's rule. Table 4 gives the comparison of calculated and tabulated values of changes of enthalpy Δ H for 6 isobars.

TABLE 4

Comparison of the values of Δ H

Isobar atm.	Range of temp. °K	ΔH_{calc}	ΔH_{Tables}	% Deviation
0.1	270 – 750	9136.0	9147	0.120
1.0	350 – 750	8219.7	8217	0.033
10.0	430 – 750	6602.2	6606	0.058
50.0	530 – 750	6518.2	6515	0.049
100.0	610 – 750	4147.2	4149	0.043
200.0	670 – 750	2248.0	2254	0.266

NOMENCLATURE

A, B, C, D,	– Constants in Equation [1].
A_1, B_1, C_1, D_1	– Constants in Equation [2].
a, b, c, d,	– Constants in Equation [4].
b_0, A_2, B_2, C_2, A_3, B_3 C_3, A_4, B_5, C_5, K	– Constants in Equation [5]
C_p	– Heat capacity at constant pressure, cal /gm. mole °K.
C_v	– Heat capacity at constant volume, cal./gm mole °K.
C_S, C_H	– Constants of integration in Equations [12] and [13] respectively.

H	– Enthalpy, cal /gm. mole.
P	– Pressure, atmospheres.
R	– Gas constant, liter atm/gm. mole °K.
S	– Entropy, cal./gm. mole °K.
T	– Temperature, °K.
V	– Specific volume, litres/gm. mole.
ΔH_0^0	– Heat of formation at 0°K, cals./gm. mole.
ΔH_v	– Enthalpy of vaporization, cals./gm mole.
ΔS_v	– Entropy of vaporization, cals /gm. mole °K.

Superscript :

*	– Properties at zero pressure or ideal gaseous state.

Subscripts :

c	– Critical point.
g	– Gas or vapour.
l	– Liquid
p	– Pressure
T	– Temperature
v	– Volume.

CHLOROFORM

TABLE 5

Properties of Saturated Liquid and Vapour

T°K	P Atm.	V_l	V_g	S_l	ΔS_v	S_g	H_l	ΔH_v	H_g
275.0	0.08921	0.07831	252.3	46.09	28.07	74.16	−27462	7719	−19743
280.0	0.1138	0.07880	201.8	46.46	27.49	73.95	−27364	7697	−19667
290.0	0.1836	0.07987	129.7	47.29	26.25	73.54	−27128	7613	−19515
300.0	0.2895	0.08091	85.02	48.18	25.03	73.21	−26860	7509	−19351
310.0	0.4296	0.08197	58.91	49.09	23.84	72.93	−26596	7390	−19206
320.0	0.6118	0.08299	42.76	49.99	22.70	72.69	−26314	7264	−19050
330.0	0.8678	0.08410	30.78	50.83	21.66	72.49	−26042	7148	−18894
340.0	1.208	0.08540	22.68	51.59	20.72	72.31	−25783	7045	−18738
350.0	1.660	0.08681	16.81	52.31	19.84	72.15	−25525	6944	−18581
360.0	2.226	0.08818	12.80	53.02	19.00	72.02	−25266	6840	−18426
370.0	2.940	0.08969	9.864	53.72	18.21	71.93	−25010	6738	−18[illegible]72
380.0	3.780	0.09132	7.796	54.43	17.43	71.86	−24742	6623	−18120
390.0	4.760	0.09311	6.280	55.15	16.65	71.80	−24463	6494	−17969
400.0	5.960	0.09488	5.073	55.88	15.89	71.77	−24177	6356	−17821
410.0	7.320	0.09681	4.171	56.62	15.13	71.75	−23878	6203	−17675
420.0	8.940	0.09811	3.437	57.36	14.37	71.73	−23569	6035	−17534

TABLE 5—(*concld*)

T°K	P atm.	V_l	V_g	S_l	ΔS_v	S_g	H_l	ΔH_v	H_g
430.0	10.83	0.1013	2.831	58.10	13.61	71.71	−23250	5852	−17[illegible]98
440 0	13.22	0.1040	2.326	58.87	12.81	71.68	−22902	5636	−17266
450.0	15 80	0.1068	1.934	59.67	11.97	71.64	−22540	5387	−17153
460 0	18 55	0.1099	1 630	60.45	11.14	71.59	−22174	5124	−17050
470 0	21.90	0.1135	1.363	61.20	10 32	71 52	−21810	4850	−16960
480.0	25 66	0 1170	1.148	62 00	9.46	71.46	−21439	4541	−16898
490.0	29.78	0.1212	0.9547	62.80	8 59	71.39	−210[illegible]8	4209	−16829
500.0	34.21	0 1264	0 8039	63.62	7.68	71.30	−20616	3840	−16776
505.0	36.58	0.1292	0.7373	64.04	7.20	71.24	−20398	3636	−16762
510.0	39 02	0.1332	0 6740	64.47	6.71	71.18	−20170	3422	−16748
515.0	41.52	0.1370	0.6154	64 91	6.18	71.09	−19936	3183	−16753
520.0	44.10	0.1424	0.5580	65.40	5.58	70.98	−19665	2902	−16763
525.0	46 81	0.1484	0.4985	65 92	4.89	70.81	−19367	2567	−16800
530.0	49.78	0.1585	0 4285	66.57	3.93	70.50	−19004	2083	−16921
535.0	52.82	0.1818	0.3133	67.55	1.99	69.54	−18401	1065	−17336
536.6	54.00	0.2388	0.2388	68.35	0.00	68.35	−17826	0·00	−17826

TABLE 6

Properties of Superheated Chloroform

Pressure range: 0.10 to 5.00 atms.

T °K	P Atms.	0.10	0.20	0.30	0.50	0.80	1.00	1.50	2.00	3.00	5.00
	V	229.1									
280.0	H	−19687									
	S	74.29									
	V	245.6	122.5	81.45							
300 0	H	−19376	−19379	−19382							
	S	75.36	73.98	73.17							
	V	262.0	130.7	86.96	51.95	32.26					
320.0	H	−19057	−19060	−19063	−19069	−19077					
	S	76.39	75.01	74.20	73.17	72.22					
	V	278 5	139.0	92.47	55.27	34.35	27.37	18.07			
340.0	H	−18729	−18732	−18734	−18740	−18748	−18754	−18769			
	S	77.39	76.01	75.20	74.18	73.23	72.78	71.95			
	V	294.9	147.2	97.98	58.59	36.44	29.05	19.20	14 27		
360 0	H	−18394	−18396	−18399	−18404	−18412	−18418	−18432	−18446		
	S	78.34	76 96	76.15	75.13	74.18	73.73	72.91	72.31		
	V	311 4	155.4	103 5	61.91	38 52	30 72	20.33	15.13	9.924	
380.0	H	−18051	−18053	−18056	−18061	−18068	−18074	−18087	−18100	−18127	
	S	79.27	77 89	77.08	76.06	75.11	74.66	73.84	73.25	72.40	

TABLE 6—(*contd*)

Pressure Range 0.10 to 5.00 atms.

T°K	P Atms.	0.10	0.20	0.30	0.50	0.80	1.00	1.50	2.00	3.00	5.00
	V	327.8	163.7	109.0	65.22	40.60	32.40	21.45	15.98	10.50	6.116
400.0	H	−17700	−17703	−17705	−17710	−17718	−17722	−17735	−17748	−17773	−17827
	S	80.17	78.79	77.98	76.96	76.02	75.57	74.74	74.15	73.31	72.22
	V	344.2	171.9	114.5	68.53	42.68	34.07	22.58	16.83	11.08	5.934
420.0	H	−17342	−17345	−17347	−17352	−17359	−17363	−17375	−17387	−17412	−17462
	S	81.04	79.66	78.85	77.83	76.89	76.44	75.62	75.03	74.19	73.10
	V	360.7	180.2	120.0	71.84	44.76	35.73	23.70	17.68	11.66	6.298
440.0	H	−16979	−16981	−16984	−16988	−16995	−16999	−17011	−17022	−17045	−17093
	S	81.89	80.51	79.71	78.68	77.74	77.29	76.47	75.88	75.05	73.97
	V	377.1	188.4	125.5	75.14	46.84	37.40	24.82	18.52	12.23	6.657
460.0	H	−16608	−16610	−16612	−16617	−16623	−16627	−16638	−16645	−16671	−16716
	S	82.71	81.33	80.52	79.50	78.56	78.11	77.29	76.71	75.87	74.80
	V	393.5	196.6	131.0	78.45	48.91	39.06	25.93	19.37	12.80	7.014
480.0	H	−16232	−16234	−16236	−16240	−16246	−16250	−16261	−16271	−16292	−16335
	S	83.52	82.14	81.33	80.31	79.37	78.92	78.10	77.52	76.68	75.61
	V	410.0	204.8	136.5	81.75	50.98	40.72	27.05	20.21	13.37	7.368
500.0	H	−15850	−15852	−15854	−15858	−15864	−15867	−15877	−15887	−15907	−15948
	S	84.30	82.92	82.11	81.09	80.15	79.70	78.89	78.30	77.47	76.40

TABLE 6—(*contd.*)

Pressure Range : 0.10 to 5.00 atms.

T°K	P atms.	0.10	0.20	0.30	0.50	0.80	1.00	1.50	2.00	3.00	5.00
520.0	V	426.4	208.9	141.9	85.05	53.05	42.38	28.16	21.05	13.94	8.245
	H	−15463	−15465	−15467	−15470	−15476	−15480	−15489	−15498	−15518	−15556
	S	85.60	83.68	82.87	81.85	80.91	80.46	79.65	79.06	78.23	77.17
540.0	V	442.8	217.2	147.4	88.35	55.12	44.04	29.27	21.89	14.50	8.593
	H	−15070	−15072	−15073	−15077	−15082	−15086	−15095	−15104	−15122	−15159
	S	85.79	84.41	83.61	82.59	81.65	81.20	80.38	79.80	78.97	77.91
560.0	V	459.3	225.4	152.9	91.65	57.19	45.70	30.39	22.73	15.07	8.939
	H	−14672	−14673	−14675	−14679	−14684	−14687	−14696	−14704	−14722	−14757
	S	86.51	85.14	84.33	83.31	82.37	81.92	81.11	80.53	79.70	78.64
580.0	V	475.7	237.7	158.4	94.95	59.26	47.36	31.50	23.56	15.63	9.284
	H	−14270	−14271	−14273	−14276	−14281	−14284	−14293	−14301	−14317	−14351
	S	87.22	85.85	85.04	84.02	83.09	82.63	81.82	81.24	80.41	79.36
600.0	V	492.1	245.9	163.9	98.25	61.32	49.01	32.60	24.40	16.19	9.627
	H	−13863	−13864	−13866	−13869	−13874	−13877	−13885	−13892	−13908	−13941
	S	87.91	86.53	85.73	84.71	83.77	83.32	82.51	81.93	81.10	80.05
620.0	V	508.5	254.2	169.4	101.5	63.39	50.67	33.71	25.23	16.75	9.970
	H	−13451	−13453	−13454	−13458	−13462	−13465	−13473	−13480	−13495	−13526
	S	88.58	87.21	86.40	85.38	84.44	84.00	83.18	82.60	81.78	80.73

TABLE 6—(*contd*)

Pressure Range: 0.10 to 5.00 atms.

T°K	P atms.	0.10	0.20	0.30	0.50	0.80	1.00	1.50	2.00	3.00	5.00
	V	525.0	262.4	174.9	104 8	65.45	52.32	34 82	26.07	17.31	10.31
640.0	H	−13036	−13038	−13039	−13042	−13047	−13049	−13057	−13064	−13078	−13108
	S	89.25	87.87	87.06	86 05	85.11	84.66	83.85	83.27	82.45	81.40
	V	541.4	270.6	180.3	108.1	67.52	53.98	35 93	26 90	17.87	10.65
660.0	H	−12618	−12620	−12621	−12624	−12628	−12631	−12638	−12645	−12659	−12687
	S	89.89	88.51	87.71	86.69	85 75	85.30	84.49	83 91	83.09	82.05
	V	557 8	278.8	185.8	111.4	69.58	55.63	37 03	27.73	18 43	10.99
680.0	H	−12195	−12197	−12198	−12201	−12205	−12207	−12214	−12221	−12234	−12261
	S	90.52	89 14	88.34	87.32	86.38	85.93	85.12	84.54	83 72	82 68
	V	574.2	287.0	191.3	114.7	71.64	57.28	38.14	28 56	18 99	11.33
700.0	H	−11770	−11771	−11773	−11775	−11779	−11782	−11788	−11795	−11807	−11833
	S	91.14	89.76	88.95	87.94	87.00	86.55	85.74	85.16	84.34	83.30
	V	590 6	295 3	196.8	118.0	73.70	58.93	39.24	29.39	19.55	11.67
720.0	H	−11341	−11342	−11344	−11346	−11350	−11352	−11358	−11365	−11377	−11402
	S	91.74	90.37	89.56	88 54	87.58	87·16	86.35	85.77	84 95	83.91
	V	615.3	307.6	205 0	123 0	76.80	61 41	40.90	30.64	20.38	12.18
750.0	H	−10692	−10693	−10694	−10697	−10700	−10703	−10708	−10714	−10726	−10749
	S	92.62	91.25	90.44	89.42	88.46	88.04	87.23	86 65	85.84	84.80

TABLE 6—(*contd.*)

Pressure Range: 8.0 to 200.0 atms.

T°K	P Atms.	8.0	10.0	15.0	20.0	30.0	50.0	80.0	100.0	150.0	200.0
	V	3.877	3.004								
420.0	H	–17544	–17603								
	S	72.04	71.51								
	V	4.116	3.204	1.972							
440.0	H	–17170	–17224	–17375							
	S	72.92	72.40	70.61							
	V	4.351	3.400	2.121	1.463						
460.0	H	–16788	–16839	–16977	–17139						
	S	73.76	73.25	71.52	71.43						
	V	4.583	3.593	2.264	1.587						
480.0	H	–16403	–16450	–16577	–16722						
	S	74.59	74.08	73.10	72.32						
	V	4.812	3.782	2.402	1.704	0.9764					
500.0	H	–16012	–16056	–16174	–16305	–16632					
	S	75.39	74.89	73.93	73.17	71.89					
	V	5.040	3.970	2.538	1.815	1.075					
520.0	H	–15617	–15658	–15768	–15888	–16172					
	S	76.16	75.67	74.72	73.99	72.79					

TABLE 6—(*contd.*)

Pressure Range: 8.0 to 200 0 atms.

T°K	P Atms.	8 0	10.0	1.50	20.0	30.0	50.0	80.0	100.0	150.0	200.0
	V	5.265	4.155	2 670	1.923	1.164	0.4859				
540.0	H	–15216	–15256	–15358	–15469	–15722	–16553				
	S	76.91	76.42	75 49	74.78	73 64	71.40				
	V	5 489	4 338	2.801	2.029	1.248	0.5867				
560.0	H	–14811	–14848	–14945	–15048	–15278	–15911				
	S	77 65	77.16	76.24	75.54	74.40	72.56				
	V	5.712	4.520	2 929	2.131	1.327	0.6620	0.2577			
580.0	H	–14403	–14438	–14529	–14625	–14836	–15369	–16749			
	S	78.37	77 88	76.97	76.29	75.22	73.52	70.61			
	V	5.933	4.701	3.056	2.332	1.403	0.7267	0.3280			
600 0	H	–13990	–14023	–14110	–14200	–14394	–14861	–15887			
	S	79.07	78.58	77.68	77.00	75.97	74 38	72.07			
	V	6.153	4.880	3.182	2.331	1.477	0.7853	0.3869	0.2718		
620.0	H	–13573	–13605	–13687	–13772	–14233	–14371	–15196	–15775		
	S	79.75	79.27	78.37	77.71	76.69	75.18	73.20	72.01		
	V	6 372	5.059	3.306	2.429	1.549	0.8398	0.4367	0 3130		
640 0	H	–13152	–13183	–13261	–13341	–13746	–13891	–14591	–85092		
	S	80.42	79.94	79.05	78.40	77.40	75.95	74.17	73.10		

TABLE 6—(*contd.*)

Pressure Range: 8 0 to 200.0 atm.

T°K	P Atms.	8.0	10.0	15.0	20.0	30.0	50.0	80.0	100 0	150.0	200.0
	V	6 590	5.236	3.429	2.525	1.619	0.8914	0.4809	0.3515	0.2213	0.1840
660.0	H	−12730	−12759	−12833	−12909	−13068	−13418	−14031	−14467	−15245	−15564
	S	81.07	80.60	79.71	79.06	73.08	76.67	75.03	74.06	72.39	71.54
	V	6.808	5.412	3.551	2.620	1.688	0.9408	0 5211	0.3871	0.2410	0.1947
680.0	H	−12302	−12330	−12400	−12472	−12622	−12946	−13495	−13880	−14635	−14995
	S	81.71	81.23	80.36	79.71	78.74	77.38	75.82	74 94	73.29	72.38
	V	7.024	5.588	3.673	2.715	1.756	0.9888	0 5585	0.4202	0.2613	0.2063
700.0	H	−11873	−11899	−11936	−12035	−12177	−12479	−12977	−13322	−14040	−14430
	S	82.33	81.86	80.99	80.34	79.39	78.05	76 58	75.75	74.16	73.20
	V	7.240	5.763	3.793	2.808	1.823	1.035	0.5939	0 4513	0.2817	0.2185
720.0	H	−11439	−11465	−11529	−11595	−11729	−12012	−12469	−12781	−13458	−13866
	S	82.94	82.47	81.60	80.97	80.02	78.71	77.29	76.51	74.98	74.00
	V	7.563	6.024	3 973	2 947	1.921	1 102	0 6439	0.4951	0 3119	0 2379
750.0	H	−10785	−10808	−10868	−10929	−11054	−11312	−11720	−11995	−12609	−13025
	S	83.83	83.36	82.50	81.87	80.94	79.66	78.31	77.58	76.13	75.14

REFERENCES

1. Beckmann, E. and Liesche, O., .. *Z. Physik. Chem.*, 1914, **88**, 23.
2. Canjar, L. N. and Manning, F. S., .. *Hydrocarbon Processing*, 1962, **41**, No. 8, 121.
3. Coop, I. E., .. *Trans. Faraday Soc.*, 1937, **33**, 583.
4. Dolezalek, F. and Schulze, A. .. *Z. Physik. Chem.*, 1913, **83**, 45.
5. Drucker, C., Jimeno, E. and Kangro, W. *Z. Physik. Chem.* 1915, **90**, 513.
6. Fischer, R and Reichel, T., .. *Mikrochemie.* 1943, **31**, 102.
7. Fletcher, J. and Tyrer, D., .. *J. Chem. Soc.* (London), 1913, **103**, 104, 517.
8. Gelles, E. and Pitzer, K.S., .. *J. Am. Chem. Soc.*, 1953, **75**, 5259.
9. Harand, J., .. *Monatsch*, 1935, **65**, 153.
10. Herz, W. and Neukirch, E., .. *Z. Physik. Chem.*, 1923, **104**, 433.
11. Herz, W. and Rathmann, W., .. *Chem. Ztg.*, 1913, **36**, 1417.
12. Kuenen, J. P. and Robson, W. G., .. *Phil. Mag.*, 1902, **4**, 121.
13. Marshall, D., .. *Phil. Mag.* 1897, **43**, 27.
14. Martin, J. J. and Hou, Y. C., .. *A. I. Ch. E. Journal*, 1955, **1**, 142.
15. Mathews, J. H., .. *J. Am. Chem. Soc.*, 1926, **48**, 562.
16. Morgan, S. O. and Lowry, H.H., .. *J. Phys. Chem.* 1930, **34**, 2385.
17. Pictet, R. and Altschul, M., .. *Z. Physik. Chem.*, 1895, **16**, 26.
18. Ramsay, W. and Aston, E., .. *Proc. Roy. Soc.* London, 1894, **56**, 182.
19. Rex, A., .. *Z Physik. Chem.*, 1916, **55**, 355.
20. Sajotschewsky, W., .. *Beibl. Ann. Physik.*, 1879, **3**, 741.
21. Scatchard, G. and Raymonds, C L., .. *J. Am. Chem. Soc.* 1938, **60**, 1278-87.
22. Schmidt, G.C., .. *Z. Physik. Chem.* 1921, **99**, 71.
23. ———, .. *Ibid*, 1926, **121**, 221.
24. Schulze, A., .. *Ibid*, 1921, **97**, 388, 417.
25. Smyth, C.P. and Morgan, S.O., .. *J. Am. Chem. Soc.*, 1928, **50**, 1547.
26. Staveley, L.A.K., Tupman, W.I. and Hart, K.R., .. *Trans. Faraday, Soc.*, 1955, **51**, 323
27. Stull, D. R , .. *Ind Eng. Chem.*, 1947, **39**, 517.
28. Thorpe, T. E., .. *Trans. Chem. Soc.*, 1880, **37**, 59.
29. Tyrer, D., .. *J. Chem. Soc.* London, 1911, **99**, 1633.
30. Vold, R. D , .. *J. Am. Chem, Soc.*, 1935, **57**, 1192.
31. Williams, J. W. and Daniels, F., .. *Ibid*, 1925, **47**, 1490.
32. Wirtz, K., .. *Ann. Physik.*, 1890, **40**, 439.
33. .. International Critical Tables, Vols. 3 and 5, McGraw-Hill, New York, 1928.