THE UNIVERSITY OF MICHIGAN
INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

THERMODYNAMIC PROPERTIES OF THE "FREON" REFRIGERANTS

I. "FREON-12" DICHLORODIFLUOROMETHANE

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September, 1955

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ACKNOWLEDGEMENT

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B.J. Eiseman, Jr.,[a] J.J. Martin,[b] R.C. McHarness[a]

I. INTRODUCTION

Twenty-four years have passed since the familiar tables of the "Thermodynamic Properties of 'Freon-12' Dichlorodifluoromethane were published (8).** These tables have served the needs of the refrigeration industry well. In 1942 they were supplemented by a set of low temperature tables and later by a table of properties of the saturated liquid and vapor at high temperatures.

Since different sets of equations were used in developing these later data, there are certain inconsistencies at their junctions with the original tables. Furthermore, some of the data at elevated pressures were based on estimations rather than on experimental data.

The primary objective of the present work has been to provide a new set of tables and charts which will meet all possible needs of the refrigeration and other industries, particularly as regards range, accuracy and consistency. We believe this has been accomplished. The steps taken to fulfill our objective were as follows: First it was necessary to review the extent and accuracy of the existing data available for "Freon-12" dichlorodifluoromethane and to make the additional measurements required. The next step was to develop a new set of equations which would fit the expanded data with the desired accuracy over the entire range. The use of this single set of equations assured the over-all consistency of the final tables and charts. In most cases it was necessary to use more complicated equations than those used for the original tables in order to obtain the desired accuracy. This was particularly true of the equation of state. The final step was to carry out the calculations and to prepare the finished tables and charts.

This paper presents the new data and equations obtained in this work. It compares the new tables with the old and describes briefly the form in which the new tables and charts are published.

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*"Freon" is the registered trademark of E.I. du Pont de Nemours and Co., Incorporated, for their fluorinated hydrocarbon refrigerants.
**Numbers in brackets refer to the bibliography at the end of the paper.

[a]"Kinetic" Laboratory, E.I. du Pont de Nemours and Co., Incorporated.
[b] Engineering Research Institute, University of Michigan.

The work reported here represents a co-operative effort of the Engineering Research Institute of the University of Michigan and the du Pont Company's Jackson and "Kinetic" Laboratories. Data from the Cryogenic Laboratory of the Pennsylvania State University were used as an independent check on the cycle calculations.

II. CALCULATION OF THE TABLES

A. Method and Criteria

1. The Cycle Calculation

The method used to calculate the tables of thermodynamic properties involved the use of the following four fundamental equations:

Vapor Pressure	$p_{sat} = f_1(T)$	(1)
Equation of State	$p = f_2(v,T)$	(2)
Density of the Saturated Liquid	$d_f = f_3(T)$	(3)
Heat Capacity of the Vapor	$c_v^0 = f_4(T)$	(4)

Exact thermodynamic relations were applied to the above empirical equations to calculate the tabular quantities. The relations in question are listed below.

$$h_{fg} = (v_g - v_f) T \frac{dp_{sat}}{dT} \tag{5}$$

$$\Delta H_v = \int_{T_1}^{T_2} c_v dT + \Delta (pv) \tag{6}$$

$$\Delta H_T = \int_{v_1}^{v_2} \left[v \left(\frac{\partial p}{\partial v} \right)_T + T \left(\frac{\partial p}{\partial T} \right)_v \right] dv \tag{7}$$

$$\Delta S_v = \int_{T_1}^{T_2} \frac{c_v}{T} dT \tag{8}$$

$$\Delta S_T = \int_{v_1}^{v_2} \left(\frac{\partial p}{\partial T} \right)_v dv \tag{9}$$

A fifth empirical equation used to represent experimental data was as follows:

Heat Capacity of the Liquid	$c_f = f_5(T)$	(10)

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This equation was used to check independently the over-all accuracy of the calculations made with equations (1) to (7).

In these calculations the pressure-volume-temperature properties of the vapor and the saturated liquid are fully determined by equations (1), (2) and (3). Latent heats of vaporization are calculated from these same equations by means of the exact Clausius-Clapeyron equation (5). The entropy of vaporization is obtained by dividing the latent heat by the absolute temperature. The other heat quantities are calculated through use of the vapor heat capacity equation (4) either alone or in combination with equation (2).

The above procedures are the same as those used by Buffington and Gilkey [8] in calculating the earlier tables.

2. Properties Required in the Basic Equations

The equations used in calculating the tables must meet four requirements. First, they must fit the experimental data accurately; that is, to the accuracy of the data themselves. Second, they must be mathematically "manageable." The calculations using them must not be unduly difficult or time-consuming. Third, the secondary or derived quantities which can be calculated from the primary data must be correct. It is possible to use an equation to represent the experimental data accurately, but which, at the same time gives unrealistic derivatives. In this connection, the fourth requirement arises. It is that the entire range of each property should be covered by a single equation. Otherwise, inconsistencies in the derived quantities will occur at the junctures of the limited-range equations.

The foregoing requirements are met by the basic equations described in the next section.

B. Basic Data and Equations

1. Scope and Accuracy

The temperature range of the observed data is from -150 to +410°F, the pressure range from 0.16 to 1980 psia. The ranges for the individual properties are shown in Tables I-V. These tables contain the experimental data which were used in the new calculations. The data and equations are discussed in the sections which follow.

The accuracy of the primary measurements varies, but is typically 1% or better. The smoothing and averaging accomplished by fitting equations to the data tends to improve the accuracy. Each equation fits the corresponding data over their entire range. This has resulted in excellent reliability of both the primary and secondary quantities calculated from the equations.

While this improved reliability is the case over a range much broader than that covered in refrigeration work, it should be pointed out that the data in the critical region are less accurate than those below this point. This is due to the rapid change in the properties of any compound near the critical point.

The "Freon-12" dichlorodifluoromethane used in making the experimental measurements was of the highest quality obtainable in our laboratory. It had a purity of not less than 99.95%.

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2. Vapor Pressure

Vapor pressures were measured by several methods [1,4]. All involved the use of an isoteniscope. There are 10 points from 0.1623 to 573.3 psia (96% of the critical pressure). The data are given in Table I. The equation below, prepared at the University of Michigan, fits these data with an average deviation of 0.22%.*

$$\log_{10} P_{sat} = 39.88381727 - \frac{3436.632228}{T}$$

$$- 12.47152228 \log_{10} T + 0.004730442244 T$$

(11)

The constants of the various equations contain as many as 10 significant figures. Fewer significant figures could have been used without loss of accuracy. However, it has been considered best to round off only in the final results in the tables, and to carry all significant figures elsewhere for the sake of maximum consistency.

Table I

Vapor Pressure of "Freon-12"**
Comparison of the Equation with Experimental Data

Temper- ature °F	Observed Pressure psia	Calculated Pressure (Eq. 11) psia	Deviation from Observed %	Source (see below)
-148.97	0.1622	0.16219	-0.01	A
-108.74	1.0200	1.0202	+0.02	A
	1.0204	1.0202	-0.02	B
-58.00	5.688	5.678	-0.18	C
-4.00	21.89	21.89	0.00	C
+32.00	44.74	44.76	+0.04	A
86.00	107.9	108.04	+0.13	C
110.08	151.8	151.27	-0.35	B
163.18	290.4	290.08	-0.11	B
176.00	331.3	334.26	+0.89	C
228.51	573.1	568.95	-0.72	A
233.6***		596.9***		

*After the vapor pressure equation (Eq. 11) had been developed, additional vapor pressure data were received in a private communication from Professor A. Michels of the University of Amsterdam. The maximum deviation of the vapor pressure equation from these data was 0.36% and the average deviation 0.30% for five points ranging between 95 and 235 psia. This excellent agreement confirms the accuracy of the vapor pressure equation.

** "Freon-12" Dichlorodifluoromethane.

***Critical point.

A. Engineering Research Institute, University of Michigan.
B. Jackson Laboratory and "Kinetic" Laboratory, E.I. du Pont de Nemours and Company, Incorporated.
C. Gilkey, Gerard and Bixler [10]. These points were calculated from the vapor pressure equation of reference [10] and used for comparison purposes.

3. Pressure-Volume-Temperature Data - Equation of State

The experimental pressure-volume-temperature data are in the form of isometrics. The pressures corresponding to a series of temperatures were determined for various loadings of a constant volume system. The apparatus and procedures are described elsewhere [1,9]. Thirty isometrics were used ranging from 1.804 to 50.53 lb/cu ft in density (0.052 to 1.515 times the critical density, d_c). The data are given in Table II.

The Martin-Hou equation of state [11] has been used to represent the data. It is satisfactory to 1.5 times the critical density. The derivation of this equation and the methods used to fit it to experimental data are described elsewhere [11]. This equation of state for "Freon-12" dichlorodifluoromethane, fitted by the University of Michigan, is as follows:

$$
\begin{aligned}
p = {} & \frac{0.088734T}{(v - b)} - \frac{3.409727134 - 1.59434848 \times 10^{-3}\,T + 56.7627671\;e^{kT_r}}{(v - b)^2} \\[2mm]
& + \frac{0.06023944654 - 1.879618431 \times 10^{-5}\,T + 1.311399084\;e^{kT_r}}{(v - b)^3} \\[2mm]
& - \frac{5.48737007 \times 10^{-4}}{(v - b)^4} + \frac{3.46883400 \times 10^{-9}\,T - 2.54390678 \times 10^{-5}\;e^{kT_r}}{(v - b)^5}
\end{aligned} \tag{12}
$$

where

$$k = -5.475;$$

$$b = 0.0065093886; \text{ and}$$

$$T_r = T/693.3.$$

Values calculated by this equation show an average deviation of 0.95% in pressure from all 114 points (on 23 isometrics) measured below the critical density.* Values from the equation have an average deviation of 2.2% from the 50 points (on seven isometrics) above the critical density.

4. Density of the Saturated Liquid

The density of the saturated liquid was determined by one of two methods [5,6]. The data are given in Table III. Calibrated floats (Faraday's method) were used for the two lowest temperatures, the three highest temperatures and the $+1.94°F$ measurement. The other points were measured with a dilatometer and reported previously [6]. The following equation fits the 18 experimental points ranging from $-187.44°F$ to $+224.06°F$ with an average deviation of 0.15%.

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*After the equation of state (Eq. 12) had been developed, new pressure-volume-temperature data were received in a private communication from Professor A. Michels of the University of Amsterdam. The maximum deviation of the equation of state from these measurements was 0.6% and its average deviation 0.2% from 38 points ranging in pressure from 104 to 327 psia and in temperature from 122 to 233°F. This excellent agreement confirms the accuracy of the equation of state.

TABLE II

"FREON-12"* PRESSURE-VOLUME-TEMPERATURE PROPERTIES
COMPARISON OF EQUATION OF STATE WITH EXPERIMENTAL DATA

Vapor Density lb/cu ft	Temper- ature °F	Observed Pressure psia	Calculated Pressure (Eq. 12) psia	Deviation from Observed %	Source (See End of Table)
61.63**	214.09	737			A
	224.46	944			
	234.14	1109			
	250.36	1424			
	261.46	1630			
	271.90	1828			
	279.05	1959			
52.62	239.29	762	757.81	-0.6	A
	254.30	948	943.21	-0.5	
	271.56	1154	1170.25	+1.4	
	286.38	1353	1375.64	+1.7	
	302.41	1551	1607.36	+3.6	
	317.55	1748	1834.32	+4.9	
	331.99	1935	2057.27	+6.3	
50.53	236.52	680	672.12	-1.2	A
	256.64	912	889.76	-2.4	
	274.28	1123	1093.47	-2.6	
	294.30	1357	1338.48	-1.4	
	312.60	1561	1570.13	+0.6	
	329.99	1767	1799.13	+1.8	
	344.30	1942	1992.51	+2.6	
49.47	233.82	645	629.77	-2.4	A
	244.02	761	730.55	-4.0	
	266.22	1005	963.95	-4.1	
	283.64	1199	1158.03	-3.4	
	301.69	1410	1367.84	-3.0	
	319.93	1627	1587.68	-2.4	
	339.60	1861	1832.35	-1.5	
45.17	259.57	847	822.20	-2.9	A
	279.93	1035	1003.67	-3.0	
	301.14	1230	1199.42	-2.5	
	320.07	1425	1379.04	-3.2	
	340.47	1636	1577.05	-3.6	
	358.70	1798	1757.34	-2.3	
	376.39	1980	1934.88	-2.3	

*"Freon-12" Dichlorodifluoromethane.
** The data at 61.63 lb/cu ft (1.8 times the critical density) lie beyond the range of the equation of state (Eq. 12).

TABLE II (cont.)

Vapor Density lb/cu ft	Temperature °F	Observed Pressure psia	Calculated Pressure (Eq. 12) psia	Deviation from Observed %	Source (See End of Table)
44.71	228.16	572	556.90	-2.6	A
	254.64	789	775.57	-1.7	
	277.70	1000	975.96	-2.4	
	299.16	1200	1169.34	-2.6	
	320.45	1400	1366.71	-2.4	
	342.54	1612	1576.41	-2.2	
	364.48	1828	1788.85	-2.1	
43.76	225.41	546	535.31	-2.0	A
	250.61	745	735.72	-1.2	
	273.06	938	922.42	-1.6	
	296.47	1146	1123.89	-1.9	
	318.58	1341	1319.50	-1.6	
	339.32	1535	1506.93	-1.8	
	361.76	1746	1713.35	-1.9	
	381.24	1930	1895.13	-1.8	
39.43	255.18	746	749.73	+0.5	A
	281.91	947	942.38	-0.5	
	307.45	1136	1129.48	-0.6	
	333.39	1331	1321.99	-0.7	
	359.06	1532	1514.50	-1.1	
	385.95	1741	1717.89	-1.3	
	408.54	1918	1889.89	-1.5	
34.72	238.38	614	626.24	+2.0	A
	272.94	830	838.27	+1.0	
	306.60	1042	1044.67	+0.3	
	336.75	1226	1229.49	+0.3	
	360.47	1371	1374.85	+0.3	
34.64	247.27	684	680.58	-0.5	B
	307.43	1027	1048.47	+2.1	
	348.11	1284	1296.99	+1.0	
	375.36	1453	1463.39	+0.7	
	386.77	1522	1533.05	+0.7	
34.38	235.19	600	606.56	+1.0	A
	239.38	638	632.00	-0.9	
	270.70	810	821.95	+1.5	
	310.77	1059	1064.49	+0.5	
	337.99	1226	1230.23	+0.3	

TABLE II (cont.)

Vapor Density lb/cu ft	Temperature °F	Observed Pressure psia	Calculated Pressure (Eq. 12) psia	Deviation from Observed %	Source (See End of Table)
32.46	210.39	467	463.81	-0.7	A
	213.03	480	479.01	-0.2	
	217.05	500	502.11	+0.4	
	237.85	608	621.10	+2.2	
	275.10	823	832.16	+1.1	
	310.27	1023	1029.56	+0.6	
	346.45	1227	1231.20	+0.3	
	387.40	1451	1458.12	+0.5	
32.41	237.30	612	617.93	+1.0	A
	250.20	685	691.17	+0.9	
	278.50	841	850.85	+1.2	
	322.20	1086	1095.23	+0.8	
	359.00	1289	1299.46	+0.8	
	392.40	1477	1483.92	+0.5	
31.73	235.70	617	608.49	-1.4	A
	261.80	750	752.84	+0.5	
	276.40	829	832.97	+0.5	
	297.20	942	946.96	+0.5	
	313.00	1027	1032.29	+0.5	
	335.00	1147	1151.20	+0.4	
	359.00	1280	1280.31	0	
20.27	250.10	630	626.57	-0.5	A
	277.50	720	711.59	-1.2	
	298.10	781	774.17	-0.9	
	315.90	833	827.46	-0.7	
	334.40	885	882.18	-0.3	
14.06	217.21	470	476.37	+1.4	A
	233.17	512	508.26	-0.7	
	291.27	613	619.92	+1.1	
	319.88	681	672.93	-1.2	
	345.70	716	719.96	+0.6	
11.94	203.76	416	421.56	+1.3	B
	244.39	477	487.18	+2.1	
	285.75	535	551.24	+3.0	
	323.83	600	612.90	+2.1	
	368.59	657	674.12	+2.6	
	410.13	715	733.96	+2.7	
10.75	222.73	424	428.26	+1.0	A
	285.92	511	514.72	+0.7	
	354.42	602	604.08	+0.3	
	383.78	640	641.47	+0.2	

TABLE II (cont.)

Vapor Density lb/cu ft	Temperature °F	Observed Pressure psia	Calculated Pressure (Eq. 12) psia	Deviation from Observed %	Source (See End of Table)
6.537	164.52	264.1	263.76	-0.1	A
	168.18	266.1	266.71	+0.2	
	199.44	298.2	291.21	-2.3	
	236.95	312.4	319.64	+2.3	
	276.05	344.7	348.42	+1.1	
5.293	149.2	219.8	218.29	-0.7	C
	175.3	236.7	234.42	-1.0	
	200.1	251.2	249.36	+0.7	
	220.3	262.8	261.29	+0.6	
	240.1	273.9	272.81	-0.4	
5.187	140.44	211.6	209.78	-0.9	B
	168.43	227.3	226.81	-0.2	
	195.30	343.2	242.68	-0.3	
	233.37	256.5	258.87	-0.9	
	248.19	273.3	272.93	-0.1	
	275.17	288.9	287.97	-0.3	
	307.12	304	305.53	+0.5	
4.756	153.0	204.8	204.08	-0.3	C
	154.9	205.7	205.12	-0.3	
	181.9	220.2	219.67	-0.2	
	210.0	235.2	234.44	-0.3	
	229.1	245.3	244.31	-0.4	
4.528	136.0	188.5	187.81	-0.4	C
	165.4	203.7	203.01	-0.3	
	180.1	210.5	210.45	0.0	
	195.1	218.4	217.94	-0.2	
	218.3	229.5	229.35	-0.1	
	240.6	240.6	240.16	-0.2	
	259.0	249.8	248.97	-0.3	
3.770	131.0	164.8	161.15	-2.2	C
	212.0	197.6	194.21	-1.7	
3.337	129.2	149.2	145.56	-2.4	C
	212.0	177.7	174.89	-1.6	
3.170	111.16	132.8	133.33	+0.4	A
	150.06	145.8	146.73	+0.6	
	203.79	162.8	164.57	+1.1	
	257.72	180.3	181.93	+0.9	
	304.34	195.3	196.66	+0.7	

TABLE II (cont.)

Vapor Density lb/cu ft	Temperature °F	Observed Pressure psia	Calculated Pressure (Eq. 12) psia	Deviation from Observed %	Source (See End of Table)
3.000	98.55	122.5	123.34	+0.7	A
	112.82	127.2	128.06	+0.7	
	162.36	142.0	143.97	+1.4	
	213.80	158.1	159.88	+1.1	
	256.28	169.9	172.72	+1.7	
	307.22	185.4	187.86	+1.3	
2.891	106.75	121.8	122.32	+0.4	A
	117.99	124.9	125.86	+0.8	
	156.58	136.4	137.72	+1.0	
	198.50	148.5	150.24	+1.2	
	275.50	170.5	172.56	+1.2	
2.821	127.4	129.2	126.17	-2.4	C
	210.2	153.6	150.37	-2.1	
2.361	127.4	110.3	108.37	-1.7	C
	210.2	130.2	128.16	-1.6	
1.804	86.0	79.5	77.79	-2.3	C
	93.2	80.9	79.13	-2.2	
	129.2	87.5	85.72	-2.0	
	210.2	102.2	100.08	-2.1	

A. Engineering Research Institute, University of Michigan.
B. Jackson Laboratory and "Kinetic" Laboratory, E.I. du Pont de Nemours and Company, Inc.
C. Buffington and Gilkey [9]. All their data are included in the above table.

$$d_f = 34.84 + 0.0269600 \ (693.3 - T) + 0.834921 \ (693.3 - T)^{1/2}$$

$$+ \ 6.02683 \ (693.3 - T)^{1/3} - 6.55549 \times 10^{-6} \ (693.3 - T)^2$$

(13)

Equation (13) was fitted at the University of Michigan.

5. Heat Capacity of the Vapor

The heat capacity of gaseous "Freon-12" dichlorodifluoromethane at zero pressure was calculated by J. F. Masi [12] from spectroscopic data, applying an anharmonicity correction based on his experimentally determined heat capacities. The results obtained in this way are reported as accurate to better than 0.15%. Masi's values for c_p^o have been converted to the corresponding values of c_v^o by subtracting 0.01642 Btu/(lb)(°F), the value of the gas constant, R. The empirical equation below, prepared at the University of Michigan, fits Masi's converted values from -150°F to +700°F with an average deviation of 0.06%, as shown in Table IV.

TABLE III

DENSITY OF LIQUID "FREON-12"*
COMPARISON OF THE EQUATION WITH EXPERIMENTAL DATA

Temp. °F	Observed Density lb/cu ft	Calculated Density (Eq. 13) lb/cu ft	Deviation from Observed %
-187.44	108.26	107.332	-0.86
-100.68	100.40	100.211	-0.19
- 36.04	94.24	94.276	+0.04
- 19.12	92.53	92.609	+0.09
- 11.02	91.70	91.793	+0.10
- 0.04	90.59	90.662	+0.08
+ 1.94	90.45	90.458	+0.01
+ 14.90	88.99	89.082	+0.10
+ 32.00	87.06	87.205	+0.17
+ 56.84	84.41	84.324	-0.10
+ 78.08	81.66	81.694	+0.04
+ 95.18	79.44	79.446	+0.01
+ 95.36	79.42	79.423	0.00
+116.42	76.54	76.442	-0.13
+133.70	73.88	73.777	-0.14
+195.98	61.09	61.162	+0.12
+210.02	56.81	56.805	-0.01
+224.06	50.82	50.452	-0.72
+233.6	34.84**	34.84	+0.00

*"Freon-12" Dichlorodifluoromethane.
** Critical density determined by extrapolating the rectilinear diameter to the critical temperature of 233.6°F.

Source: Jackson Laboratory and "Kinetic" Laboratory, E.I. du Pont de Nemours and Company, Incorporated.

TABLE IV

"FREON-12"* VAPOR HEAT CAPACITY
COMPARISON OF EQUATION WITH MASI'S DATA [12]

Temp. °F	c_v^o Masi Btu/(lb)(°F)	Calculated c_v^o (Eq. 14) Btu/(lb)(°F)	Deviation from Masi %
-150.0	0.0899	0.08997	+0.08
- 99.7	0.0997	0.09971	+0.01
+ 32.0	0.1213	0.12129	-0.01
+ 80.3	0.1279	0.12793	+0.02
+260.3	0.1476	0.14757	-0.02
+440.3	0.1611	0.16098	-0.07
+620.3	0.1705	0.17051	+0.01
+700.0	0.1737	0.17411	+0.24

*"Freon-12" Dichlorodifluoromethane.

$$c_v^o = 0.0080993 + 3.32662 \times 10^{-4}T - 2.413896 \times 10^{-7}T^2 + 6.72363 \times 10^{-11}T^3 \quad (14)$$

6. Heat Capacity of the Saturated Liquid

Heat capacity data have been published by Riedel [13]. More recently the heat capacity of the saturated liquid was determined calorimetrically at the Pennsylvania State University using methods previously described [2]. These latter data are given in Table V. The seventeen points between -155.5°F and -3.5°F show an average deviation of 0.20% from the following equation prepared by the Pennsylvania State University:

$$c_f = 0.195881 - 0.118739 \times 10^{-3}T + 0.361742 \times 10^{-6}T^2 \quad (15)$$

TABLE V
HEAT CAPACITY OF LIQUID "FREON-12"*
COMPARISON OF THE EQUATION WITH THE DATA

Temp. °F	Observed Heat Capacity Btu/(lb)(°F)	Calculated Heat Capacity (Eq. 15) Btu/(lb)(°F)	Deviation from Observed %
-155.50	0.1934	0.19322	-0.09
-146.52	0.1940	0.19421	+0.11
-127.71	0.1969	0.19636	-0.27
-127.74	0.1966	0.19636	-0.12
-117.77	0.1974	0.19744	+0.02
-108.70	0.1993	0.19876	-0.27
- 99.61	0.2000	0.20000	0.00
- 90.52	0.2026	0.20132	-0.63
- 82.06	0.2027	0.20265	-0.03
- 69.96	0.2044	0.20455	+0.07
- 60.64	0.2065	0.20612	-0.19
- 52.07	0.2069	0.20761	+0.34
- 42.39	0.2085	0.20935	+0.41
- 32.43	0.2106	0.21117	+0.27
- 23.18	0.2127	0.21299	+0.14
- 13.14	0.2155	0.21497	-0.25
- 3.53	0.2174	0.21696	-0.20

*"Freon-12" Dichlorodifluoromethane.

Source: Cryogenic Laboratory, the Pennslyvania State University.

7. Critical Constants

The critical constants were measured as follows: the critical temperature was determined to be 233.6°F by observing the temperature of disappearance of the surface separating the liquid and gas. The critical pressure was determined as 596.9 psia by substituting the critical temperature in the vapor pressure equation (Eq. 11). The critical density was determined as 34.84 lb/cu ft by extrapolating the rectilinear diameter to the critical temperature.

C. Over-all Accuracy of the Calculated Results

The heat capacity of the saturated liquid (Section B,6) provides independent data for checking the accuracy of the cycle calculation. In effect, the cycle calculation has brought us from the reference point on the saturated liquid line at -40°F (419.7°R) through the properties of the vapor back to another point on the saturated liquid line. As a result, any errors in the cycle calculations have been accumulated in the liquid enthalpy values. The over-all accuracy of the results obtained by cycle calculations can be checked by comparing the above liquid enthalpy values with the values based on direct experimental data, calculated using the following equation:

$$\Delta h_f = \int_{419.7}^{T_2} c_f dT + \int_{p_1}^{p_2} v_f dp_{sat} \ . \tag{16}$$

The required values of c_f* are given by equation (15). The quantity

$$\int_{p_1}^{p_2} v_f dp_{sat}$$

was evaluated as $[(v_{f_2} + v_{f_1})/2] \Delta p_{sat}$. This procedure introduced only negligible error since the term is small and the change in v_f with saturation pressure is almost linear in the range in question.** Liquid enthalpy values calculated in this way are compared with values from both the new and old tables in Table VI.

TABLE VI

ENTHALPY OF LIQUID "FREON-12"[†]
COMPARISON OF OLD AND NEW TABLES WITH INDEPENDENT DATA

Temp. °F	Enthalpy, h_f, Based on Observed Data (Eq. 15) Btu/lb	New Tables		Old Tables [3,8]	
		Enthalpy, h_f Btu/lb	Deviation from Observed %	Enthalpy, h_f Btu/lb	Deviation from Observed %
-150	-22.098	-22.697	-2.7	-23.50	-6.3
-120	-16.234	-16.565	-2.0	-16.94	-4.3
- 80	- 8.238	- 8.345	-1.3	- 8.40	-2.0
- 40	0	0	0	0	0
0[††]	+ 8.519	+ 8.521	0.0	+ 8.25	-3.2

[†] "Freon-12" Dichlorodifluoromethane.
[††] Upper temperature limit of the experimental data.

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*The quantity measured experimentally was:

$$c_f = \left(\frac{\delta Q}{dT}\right)_{sat} = T\left(\frac{dS}{dT}\right)_{sat} = \left(\frac{dh_f}{dT}\right)_{sat} - v_f\left(\frac{dp}{dT}\right)_{sat} \tag{17}$$

**An exact evaluation of $\int_{p_1}^{p_2} v_f dp_{sat}$ could be made by using the vapor pressure equation (Eq. 11) and the liquid density equation (Eq. 13).

Over the range of the experimental data, from -150°F to 0°F, the deviation of the new tables from these independent data does not exceed 2.7%. The deviations are progressively smaller toward the higher temperatures. The old tables are in definitely poorer agreement with the experimental data than the new.

D. Comparison of the Old Tables with the New

The old tables have been compared with the new over the entire range that is common to both. The results are presented in the form of a series of eight difference curves (Figures 1 to 5) which are discussed below. In Figures 1 and 2 the curves are the deviations of the values in the old tables from the corresponding values in the new tables. These latter values are represented by the zero base line. It should be noted that the deviations might be expected to be relatively large at pressures above 220 psia, since the old data in this range were based on a combination of estimated and experimental quantities.

Figures 1 and 2 compare several properties at saturation. Figure 1-A shows that the old and new tables agree very well in saturation pressure, particularly in the region of the original tables [8]. (For easy reference the region of the original tables -40 to +140°F, has been set off by vertical dotted lines.) Figure 1-B shows very close agreement for the density of the liquid except near the critical point. Figure 1-C, on the other hand, indicates that deviations in the latent heat are from less than 1% to almost 3% in the refrigeration range. The reason for this is that the volumes in the old tables are too high (see Figure 3, discussed below), so that latent heats, calculated from the Clapeyron equation (Eq. 6) are also too high.

The deviations in Figure 1 are given in per cent. In Figure 2, deviations in the enthalpy and the entropy of the liquid are given in absolute values. The reason for doing so is that these values are zero at -40°F so that a very small deviation leads to an enormous percentage near this temperature. However, to give the reader an understanding of the relative size of the deviation, percentage figures have been written in at high and low points on the deviation curves. It is seen that in both cases the absolute deviations are not large in the -40°F to +140°F region. The deviation plot for the enthalpy, Figure 2-A, extends the comparison already made in Table VI, to higher temperatures.

Figures 3, 4 and 5 show deviations for the vapor volumes, enthalpies and entropies, both at saturation and in the superheat. The deviations are shown by means of contour lines on a pressure versus temperature graph. A contour line is drawn at each 0.5% of deviation of the values in the old tables from the corresponding values in the new tables.

In Figure 3, it is seen that vapor volumes were as much as 3.5% too high at the higher pressures in the old tables. This is the major point of difference between the old and new tables. It arises from the higher pressures obtained for the low density isometrics at the University of Michigan as compared with those reported by Buffington and Gilkey (see bottom of Table II). The correctness of the more recent values has been confirmed by comparison with the independent data of Professor A. Michels, as pointed out previously. The considerable effect of these differences in volume values on the latent heats of vaporization was shown in Figure 1-C.

Figure 4 shows that the old tables agree very well with the new as regards vapor enthalpies. That this is also the case for the vapor entropies is shown in Figure 5.
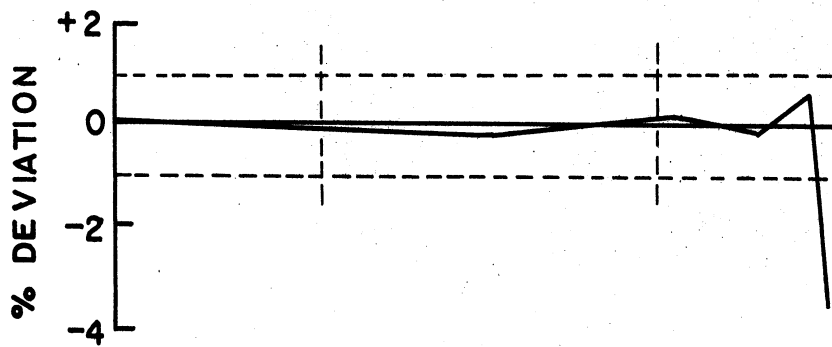
FIGURE 1
DEVIATION OF THE OLD TABLES FROM THE NEW

A. VAPOR PRESSURE
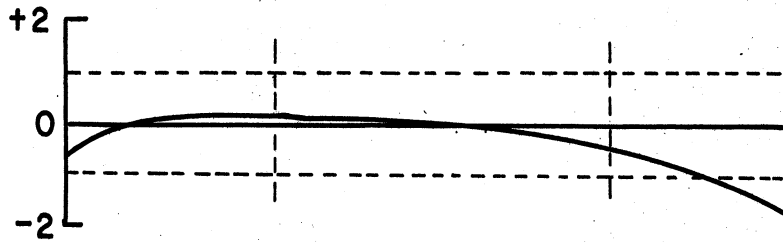
B. LIQUID DENSITY

C. ENTHALPY OF VAPORIZATION
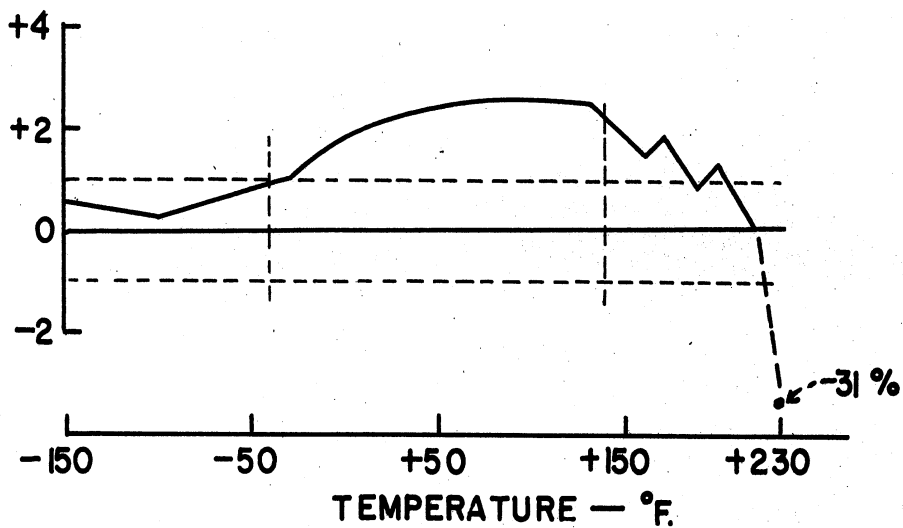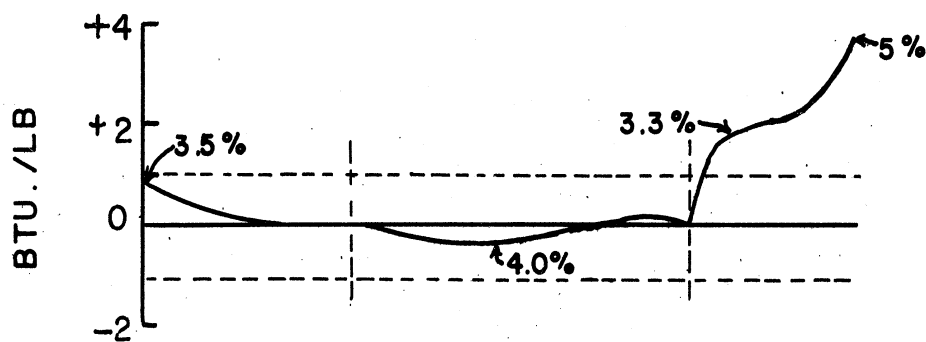
TEMPERATURE — °F.

FIGURE 2

DEVIATION OF THE OLD TABLES FROM THE NEW

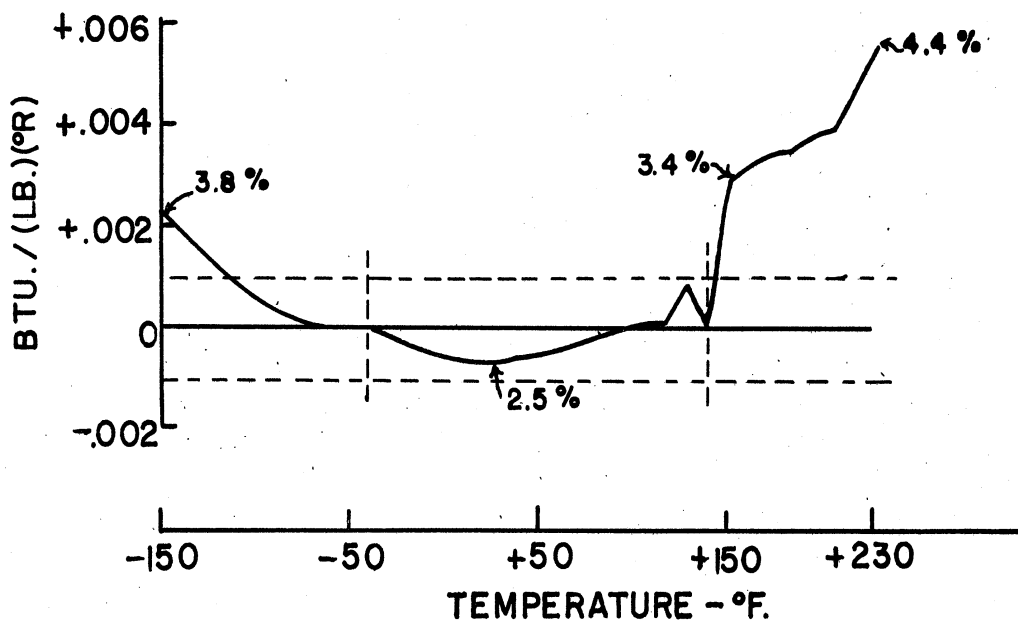### A. ENTHALPY OF THE LIQUID

B. ENTROPY OF THE LIQUID

FIGURE 3
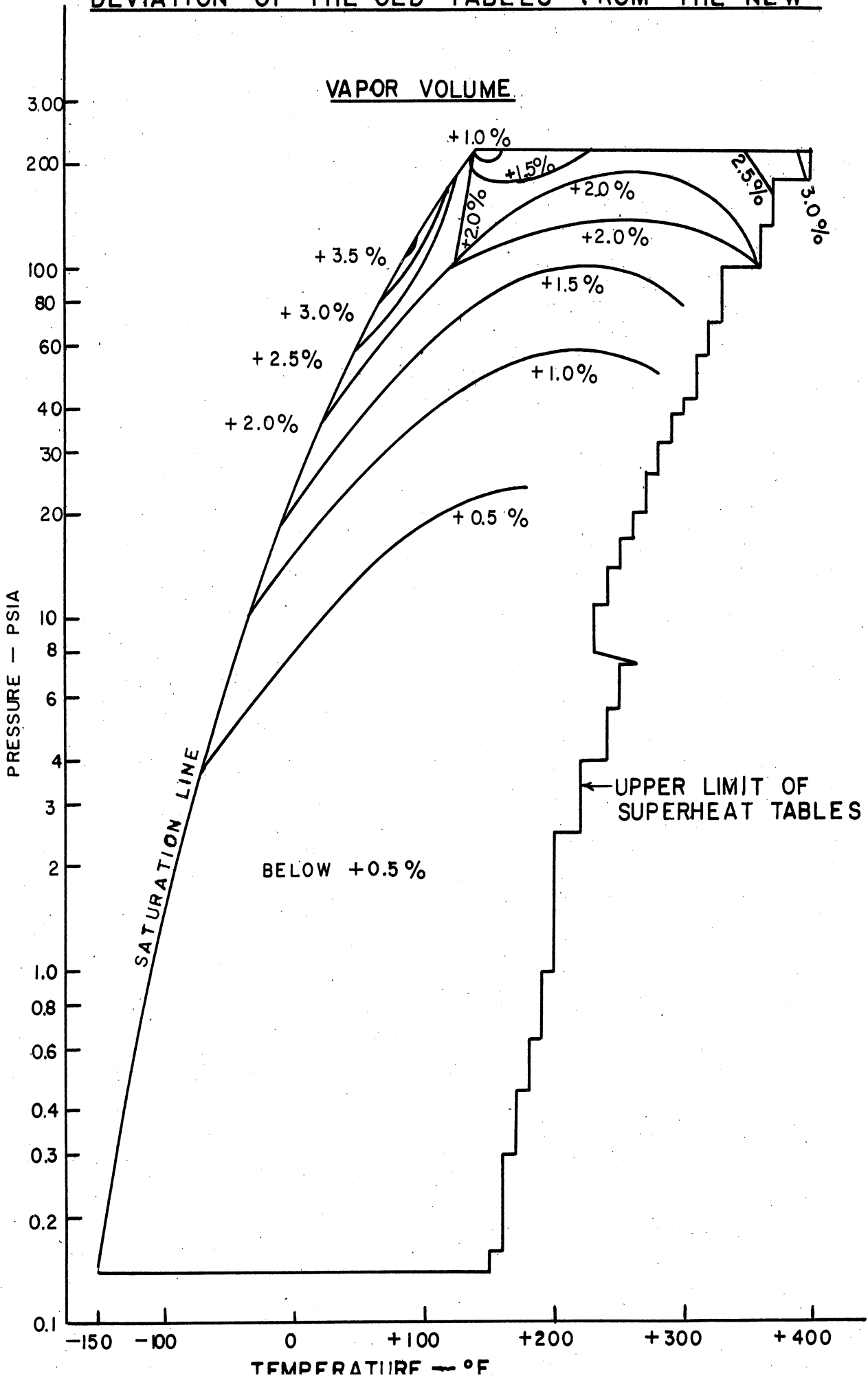DEVIATION OF THE OLD TABLES FROM THE NEW

VAPOR VOLUME

FIGURE 4
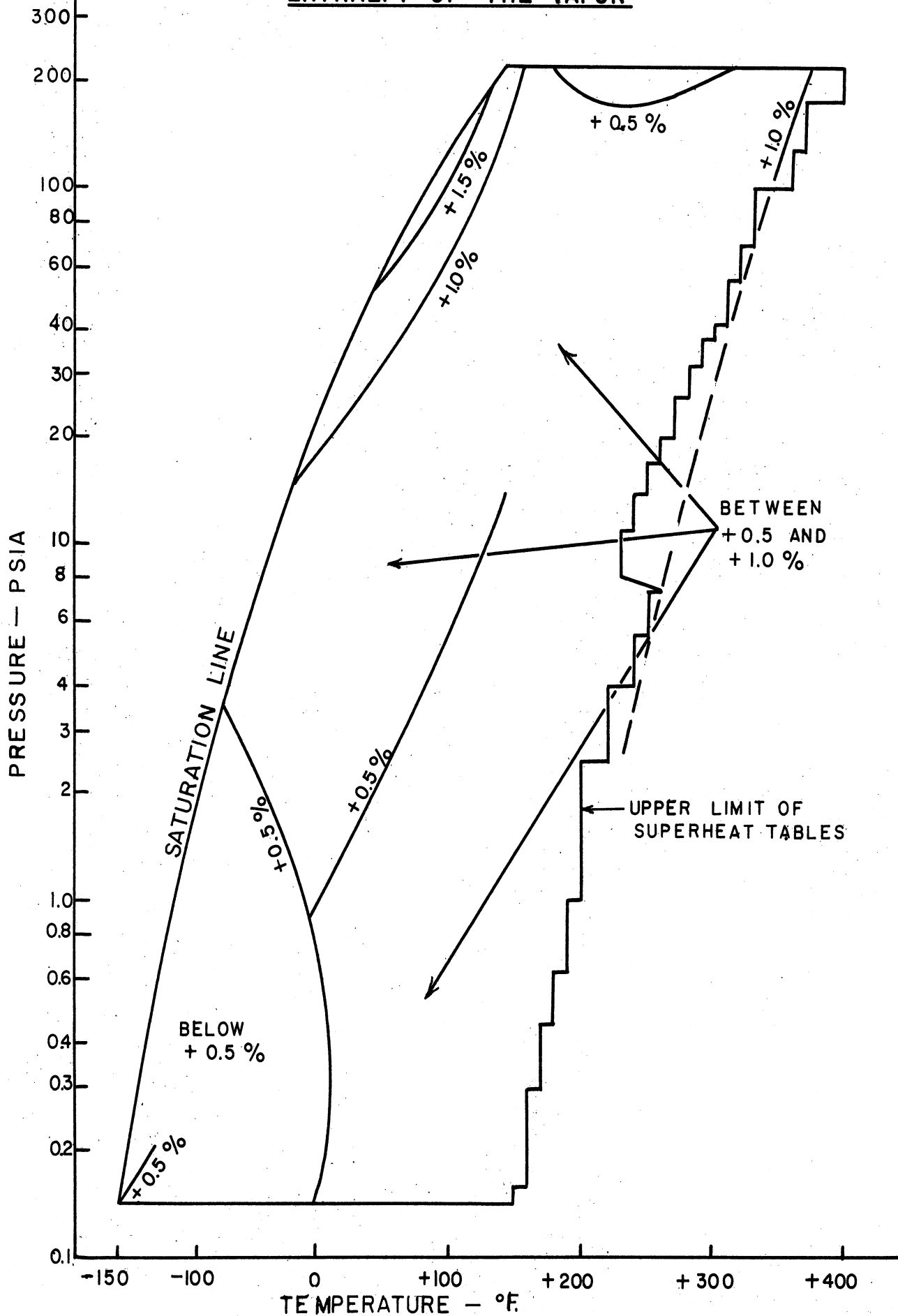
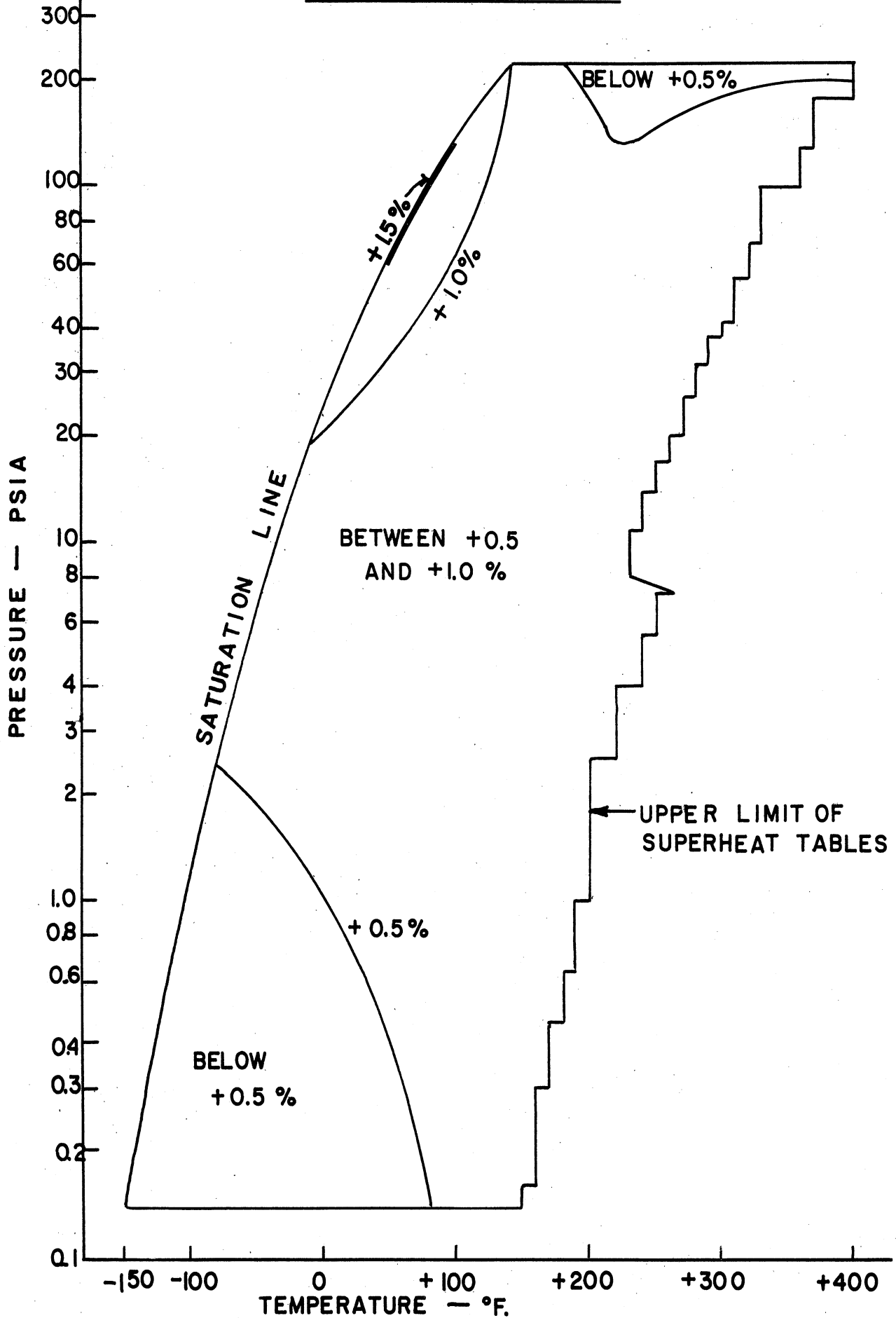DEVIATION OF THE OLD TABLES FROM THE NEW

ENTHALPY OF THE VAPOR

FIGURE 5

DEVIATION OF THE OLD TABLES FROM THE NEW

ENTROPY OF THE VAPOR

The standard ton characteristics given by the old and new tables are compared in Table VII. As would be expected from the differences shown in Figures 1 to 4, the largest differences occur in the vapor volumes, latent heat and net refrigerating effect. However, the compressor displacement per ton of refrigeration is not changed significantly.

TABLE VII

"FREON-12"* STANDARD TON CHARACTERISTICS
COMPARISON OF THE OLD AND NEW TABLES

	New	Old	Deviation from New %
Evaporator Pressure at 5°F, psia	26.483	26.51	+0.1
Condenser Pressure at 86°F, psia	108.04	107.9	-0.1
Compression Ratio (86°F/5°F)	4.08	4.07	-0.2
Latent Heat of Vaporization at 5°F, Btu/lb	68.204	69.47	+1.0
Net Refrigerating Effect, Btu/lb	50.035	51.07	+1.0
Refrigerant Circulated per Ton of Refrigeration, lb/min	3.9972	3.916	-2.0
Saturated Liquid Volume at 86°F, cu ft/lb	0.012396	0.0124	0.0
Liquid Circulated per Ton of Refrigeration, cu in./min	85.621	83.91	-2.0
Saturated Vapor Density at 5°F, lb/cu ft	0.68588	0.6735	-1.9
Saturated Vapor Density at 86°F, lb/cu ft	2.6556	2.569	-3.3
Compressor Displacement per Ton of Refrigeration, cu ft/min	5.8279	5.815	-0.2
Refrigeration per Cubic Foot of Compressor Displacement, Btu	34.318	34.39	+0.2

*"Freon-12" Dichlorodifluoromethane.

E. The Numerical Calculation

1. Constants and Conversion Factors

The molecular weight of "Freon-12" dichlorodifluoromethane was taken as 120.93. The gas constant used was 10.731 (psia)(cu ft)/(°R)(lb mole). The factor used in converting work units [(psia x cu ft)/lb] to heat units (Btu/lb) was 0.18505. One atmosphere was taken as 14.696 psia. The Rankine temperature was taken as °F + 459.7. The enthalpy and entropy of the saturated liquid at -40°F were taken as zero.

2. The Use of an Electronic-Calculating Machine

In extending the range of the tables, it was necessary to use more complex equations to obtain the desired accuracy. This would not have been feasible with a manual calculating machine. The new tables have been calculated on an electronic machine, the International Business Machines Corporation No. 701.

It has allowed the use of a far more complicated equation of state than would have been practical heretofore. The calculation of some 150,000 values required only about 30 hours of machine time. The rapidity of the calculation permitted the testing of variants in some of the equations by using them to calculate sections of the tables. Choices in some instances were based on a comparative study of the tabular results. Thus, the use of the machine greatly improved the flexibility of the calculations as well as the speed.

About 40,000 individual values appear in the published tables. The other numerical values were used in preparing the charts and certain unpublished tables. The IBM machine calculated ten significant figures. However, five significant figures are sufficient not only for fixing the tabular values, but also for determining trends in the differences between tabular values which are frequently of interest to the refrigerating engineer. For these reasons and for the sake of compactness and ease of use, only five significant figures are included in the tables. If additional figures are required in special cases, it will be possible to supply them. This is true of both the published and unpublished values. It applies, for example, to values of c_p, c_v and their ratio, which are published only in the form of small graphs.

III. THE NEW TABLES*

A. General

Since the tables have been extended considerably and since a number of large charts are included with them, they are, for convenience, wire-bound in book form, 8-1/2" x 11" in dimensions. The new tables include the same quantities as the old tables. Values are reported to five significant figures, however, instead of to the four figures used earlier.

The complete tables consist of three saturation tables (even temperature, even absolute pressure, even gage pressure) followed by two groups of superheat tables (even absolute pressure, even saturation temperature). They are described below.

B. The Saturation Tables

All three saturation tables list values for each of the quantities reported in the old tables; namely, temperature, absolute pressure, gage pressure, volume of the liquid, volume of the vapor, density of the liquid, density of the vapor, enthalpy of the liquid, enthalpy of vaporization, enthalpy

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*The new tables and charts will be made available to everyone who has need of them. They will be ready for distribution about December 1, 1955.

of the vapor, entropy of the liquid and entropy of the vapor. The old saturation table is at 2°F intervals of temperature. The new even temperature value table has a 1°F interval and a range from -152 to +232°F.

The saturation values are also reported at even values of absolute pressure and even values of gage pressure. There are about the same number of entries in each of these tables as in the even temperature value table. These even pressure tables have been added to eliminate the inconvenience of interpolation and to co-ordinate with the even pressure value superheat tables.

C. The Superheat Tables

The even pressure value tables list the volume, enthalpy and entropy of the superheated vapor at constant pressure at even 10°F temperature intervals just as in the old tables. The pressure range of the new tables is from 0.14 to 500 psia (-152 to +215°F at saturation) and the tables extend 300°F into the superheat. Of the 172 tables of this type calculated, 129 are published. These lie mainly in the refrigeration range.

The second set of constant pressure tables consists of individual tables at even values of the saturation temperature. The arrangement, quantities and intervals in the individual tables are the same as in the first set. The same range is covered in 126 tables. This form of table co-ordinates directly with the even temperature value saturation table.

IV. THE NEW CHARTS*

A. General

In general, charts serve a twofold purpose. They cover broad ranges of data compactly and they provide a convenient means for calculating cycles rapidly. The range and number of charts have been chosen with these purposes in mind so as to meet the needs of refrigerating engineers and other users of "Freon-12" dichlorodifluoromethane as well.

There is a broad-range pressure-enthalpy chart, extending beyond the limits of the printed tables and covering all available data. A second chart gives the refrigeration range in greater detail. The refrigeration range is also covered by an eight-part sectional chart on a very large scale.

There are, in addition, an entropy-enthalpy diagram and charts of the specific heats and their ratio. The charts are described below.

B. Pressure-Enthalpy Diagrams

The broad-range pressure-enthalpy diagram covers the range from 0.14 to 5000 psia in pressure, -150 to +700°F in temperature and extends vapor volumes to as low as 0.019 cu ft/lb (equivalent to 1.5 times the critical density).

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*The new tables and charts will be made available to everyone who has need of them. They will be ready for distribution about December 1, 1955.

This chart is about 20" x 22" in size. There is a chart of the refrigeration range which covers pressures from 9 to 500 psia (-40 to +215°F at saturation) and extends to about 450°F. It is in color and has a size of about 17" x 23".

The eight-part sectional chart of the refrigeration range covers the same region as the refrigeration chart discussed above. Each section is approximately 10" x 34" and folds to fit in the 8-1/2" x 11" book of tables. The enlarged scales of these sectional charts make it possible to read them with a high degree of accuracy. For example, the smallest scale division of enthalpy is 0.05 Btu/lb so that it will be possible to estimate enthalpies to 0.01 Btu/lb. Thus, this graph should be of great utility where cycle calculations of high accuracy are required.

C. Entropy-Enthalpy Diagram

The entropy-enthalpy diagram covers the same range as the broad range pressure-enthalpy diagram, but with entropy as abscissa and enthalpy as ordinate. The smallest division on the enthalpy scale is 0.1 Btu/lb so that it will be possible to estimate to 0.02 Btu/lb. The size of this chart is about 20" x 45".

D. Graphs of the Specific Heat Data

Three graphs give respectively c_p, c_v and their ratio over the entire range of the data.

V. ACKNOWLEDGEMENTS

Mr. R. B. Ramsey of du Pont's "Kinetic" Laboratory for his tireless efforts in laying out the plans for the various tables and charts.

Mr. K. R. Weigand of South Bend, Indiana, for preliminary calculations and his exceptional craftsmanship in the drawing of the charts and diagrams.

VI. CONCLUSION

Data have been developed and equations derived for the purpose of calculating a new set of tables and charts of the thermodynamic properties of "Freon-12" dichlorodifluoromethane. The finished tables and charts represent the co-operative effort of several laboratories and numerous individuals. They are based both on the new data and the old data as well. Greater accuracy has been attained and a broader range has been covered than heretofore. It is expected that the requirements of refrigerating engineers and other users will be satisfied by these tables and charts for many years.

VII. REFERENCES

1. L. F. Albright and J. J. Martin, Ind. Eng. Chem. 44, 188-189 (1952).

2.a. J. G. Aston and G. H. Messerly, J. Am. Chem. Soc. 58, 2354 (1936).

  b. Messerly and Aston, Ibid., 62, 886 (1940).

3. A. F. Benning and W. H. Markwood, "Thermodynamic Properties of 'Freon-12' at Low Pressures," "Kinetic" Chemicals Division, 1942.

4. A. F. Benning and R. C. McHarness, Ind. Eng. Chem. 32, 497-99 (1940).

5. A. F. Benning and R. C. McHarness, Ibid., 32, 814-16 (1940).

6. F. R. Bichowsky and W. K. Gilkey, Ibid., 23, 366 (1931).

7. R. M. Buffington and J. Fleischer, Ibid., 23, 1290 (1951).

8. R. M. Buffington and W. K. Gilkey, "Thermodynamic Properties of 'Freon-12' Dichlorodifluoromethane," American Society of Refrigerating Engineers Circular No. 12, (1931).

9. R. M. Buffington and W. K. Gilkey, Ind. Eng. Chem. 23, 254 (1931).

10. W. K. Gilkey, F. W. Gerard and M. E. Bixler, Ibid., 23, 364 (1931).

11. J. J. Martin and Y. C. Hou, "Development of a New Equation of State for Gases," A.I.Ch.E. Journal, 1, No. 2 (1955).

12. J. F. Masi, J. Am. Chem. Soc. 74, 4738 (1952).

13. L. Riedel, Z. für die gesamte Kälte-Industrie 46, 105-6 (1939).

VIII. NOMENCLATURE

h_{fg} = enthalpy of vaporization in Btu/lb,

h_f = enthalpy of the saturated liquid in Btu/lb,

h_g = enthalpy of the saturated vapor in Btu/lb,

h = enthalpy of the superheated vapor in Btu/lb,

H = enthalpy,

v = volume in cu ft/lb,

t = temperature in $^\circ F$,

T = absolute temperature in $^\circ R = t^\circ F + 459.7$,

p = absolute pressure in psia,

p_d = gage pressure in psig,

S = entropy in Btu/(lb)($^\circ R$),

s_{fg} = entropy of vaporization in Btu/(lb)($^\circ R$),

s_f = entropy of the saturated liquid in Btu/(lb)($^\circ R$),

s_g = entropy of the saturated vapor in Btu/(lb)($^\circ R$),

c_v^0 = specific heat at constant volume at zero pressure, Btu/(lb)($^\circ F$),

c_v = specific heat at constant volume in Btu/(lb)($^\circ F$),

c_p = specific heat at constant pressure in Btu/(lb)($^\circ F$),

c_f = specific heat of saturated liquid in Btu/(lb)($^\circ F$),

b = equation of state constant = 0.0065093886 cu ft/lb

k = equation of state constant = -5.475,

T_r = reduced temperature = $T/693.3$,

d = density in lb/cu ft,

Q = heat added to the system.

Subscripts

r = reduced,

c = critical,

f = liquid,

sat = saturated,

g = saturated vapor,

T = constant temperature,

v = constant volume,

p = constant pressure.

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