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DATA AND EQUATIONS FOR SOME THERMODYNAMIC PROPERTIES  
"FREON-12" DICHLORODIFLUOROMETHANE

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OBJECTIVE

The objective of this project is to determine the thermodynamic properties of "Freon" refrigerants.

## INTRODUCTION

The purpose of this report is to present the information necessary for the calculation of a table of thermodynamic properties (pressure, temperature, volume, enthalpy, and entropy) for the saturated liquid, saturated vapor, and superheated gas of "Freon-12" dichlorodifluoromethane.

Some new findings and a complete summary of published data, including the vapor pressure, the density and heat capacity of the saturated liquid, the PVT behavior and heat capacity of the gas, the normal boiling point, and the critical temperature, pressure and volume are presented. The thermodynamic consistency of the vapor pressure equation, equation of state, and the liquid and vapor heat capacities for this compound are also discussed. The variation of heat capacity ( $C_p$ ) of the gas with pressure is evaluated from the equation of state.

## RESULTS

## 1. CRITICAL PROPERTIES AND NORMAL BOILING POINT

A. Critical temperature was determined at Jackson Laboratory and reported by Whitney.<sup>12</sup> This temperature is 233.6°F or 693.3°R, where absolute zero is taken as -459.7 °R.

B. The critical pressure was calculated by inserting the critical temperature into the vapor pressure equation and found to be 596.9 psia.

C. The critical density (34.84 lb/cu ft) was determined by a rectangular diameter of temperature versus saturated liquid or gas density.

D. The normal boiling point was calculated as -21.92°F or 438.08°R, by solving the recommended vapor pressure equation at a pressure of 14.696 psia.

2. SATURATED LIQUID DENSITY ( $d_L$ )

Density of the saturated liquid is presented in two alternate forms of equations. The first was reported by Eiseman;<sup>4</sup> the second is consistent with our previous report on "Freon" refrigerants and is recommended for use in the determination of tables of thermodynamic properties. The observed data were obtained from Jackson Laboratory.<sup>6,9</sup>

$$I. d_L = 34.84 + 18.0048 (1-T/693.3) + 74.1153 (1-T/693.3)^{0.36643}$$

$$II. d_L = 34.84 + 0.0269600 (693.3-T) + 0.834921 (693.3-T)^{1/2} + 6.02683 (693.3-T)^{1/3} - 6.55549 \times 10^{-6} (693.3-T)^2$$

$$d_L = \text{lb/cu ft}$$

TABLE I  
COMPARISON OF EXPERIMENTAL AND CALCULATED SATURATED LIQUID DENSITIES

Temp °F	$d_L$ obs.	$d_L$ calc.(I)	Deviation %	$d_L$ calc.(II)	Deviation %
-187.44	108.263	107.511	-.70	107.332	-.87
-100.68	100.403	100.252	-.15	100.211	-.19
- 36.04	94.235	94.278	+.05	94.276	+.04
- 19.12	92.531	92.608	+.08	92.609	+.08
- 11.02	91.700	91.790	+.10	91.793	+.10
- 0.04	90.589	90.660	+.08	90.662	+.08
+ 1.94	90.452	90.454	+.00	90.458	+.01
+ 14.90	88.985	89.082	+.11	89.082	+.11
+ 32.00	87.062	87.211	+.17	87.205	+.16
+ 56.84	84.409	84.348	-.07	84.324	-.10
+ 78.08	81.662	81.738	+.09	81.694	+.04
+ 95.18	79.440	79.503	+.08	79.446	+.01
+ 95.36	79.421	79.479	+.08	79.423	+.00
+116.42	76.537	76.520	-.02	76.442	-.12
+133.70	73.877	73.877	0	73.777	-.14
+195.98	61.086	61.296	+.34	61.162	+.12
+210.02	56.809	56.923	+.20	56.805	-.01
+224.06*	50.816*	50.499	-.62*	50.452	-.72*
+233.6	34.84	34.84	0	34.84	0
Average deviation			0.16	0.15	
Average deviation (excluding 1st and 2nd to last points)			0.09	0.08	

\*This point lies out of line on a smooth curve graph.

3. SATURATED LIQUID HEAT CAPACITY ( $C_S^l$ )

Heat capacities for liquid along the saturation line ( $C_S^l$ ) were represented by an equation given in a confidential report by J. G. Aston.<sup>1</sup> The equation fits his data within 0.5% deviation over the range of temperatures from 216°R to 455°R.

$$C_S^l = 23.682 - 0.02584T + 0.0001417T^2 \frac{\text{cal}}{\text{mole } ^\circ\text{K}}$$

$$T = ^\circ\text{K} .$$

Converting this equation to engineering units,

$$C_S^l = 0.195708 - 1.1864 \times 10^{-4}T + 3.6142 \times 10^{-7}T^2 \frac{\text{Btu}}{\text{lb } ^\circ\text{R}}$$

$$T = ^\circ\text{R} .$$

4. GAS HEAT CAPACITIES

Masi<sup>8</sup> measured ideal gas heat capacities for "Freon-12". A four-constant equation was used to represent his data over the temperature range shown in Table II. The constants were evaluated by requiring the equation to reproduce the observed values at four temperatures.

The equation for  $C_V^0$  differs from  $C_P^0$  by R equal to  $1.98589 \frac{\text{Btu}}{\text{lb mole } ^\circ\text{R}}$  or  $0.0164225 \frac{\text{Btu}}{\text{lb } ^\circ\text{R}}$  .

A. Constant-pressure heat capacity for the ideal gas:

$$C_P^0 = 0.0245028 + 3.32442 \times 10^{-4}T - 2.412299 \times 10^{-7}T^2 + 6.719186 \times 10^{-11}T^3 \frac{\text{Btu}}{\text{lb } ^\circ\text{R}} .$$

B. Constant-volume heat capacity for the ideal gas:

$$C_V^0 = 0.0080803 + 3.32442 \times 10^{-4}T - 2.412299 \times 10^{-7}T^2 + 6.719186 \times 10^{-11}T^3 \frac{\text{Btu}}{\text{lb } ^\circ\text{R}} .$$

Here T is in °R. The degree sign (°) on the heat capacities indicates zero pressure or ideal gas state.

TABLE II

IDEAL GAS HEAT CAPACITY ( $C_p^0$ ) FOR "FREON-12"

Temp °K	$C_p^0$ obs. cal/mole °K	$C_p^0$ calc. cal/mole °K	Deviation %	Experimental Investigator
200	14.043*	14.043	0	8
273.16	16.654	16.653	0	8
300	17.456*	17.456	0	8
400	19.831*	19.831	0	8
500	21.469	21.452	-.08	8
600	22.605*	22.605	0	8
700	23.411	23.573	.70	8

\* Equation fitted through this value.

## 5. PVT RELATIONSHIPS OF THE GAS

The Martin-Hou<sup>7</sup> equation of state was used to correlate the PVT data. The following values were used to evaluate the constants in the equation:

$$\begin{aligned}
 R &= 10.73 \text{ psia-ft}^3/\text{lb mole-}^\circ\text{R}, \\
 \text{Mol.wt.} &= 120.924 \text{ lb/lb mole}, \\
 P_c &= 596.9 \text{ psia}, \\
 T_c &= 693.3^\circ\text{R}, \\
 T_B &= 1570^\circ\text{R}, \\
 T' &= 554^\circ\text{R}, \\
 \beta &= 3.23, \\
 m &= 6.16, \\
 \underline{V}_c &= 0.0287026406 \text{ ft}^3/\text{lb}, \\
 \underline{Z}_c &= 0.278456844, \\
 b &= 0.0065093886 \text{ ft}^3/\text{lb}, \\
 \frac{d^2P}{dT^2} &= 0 \text{ at } 2.5 \text{ times the critical density.}
 \end{aligned}$$

Summary of the Formulae and Procedures  
for Evaluating the Arbitrary Constants  
in the Martin-Hou Equation of State with a  $C_5$  Term

Equation of state:

$$P = \frac{RT}{\underline{V}-b} + \frac{A_2+B_2T+C_2e^{-5.475\frac{T}{T_c}}}{(\underline{V}-b)^2} + \frac{A_3+B_3T+C_3e^{-5.475\frac{T}{T_c}}}{(\underline{V}-b)^3} + \frac{A_4}{(\underline{V}-b)^4} + \frac{B_5T+C_5e^{-5.475\frac{T}{T_c}}}{(\underline{V}-b)^5}$$

Formulae (in order of Evaluation):

$$b = \frac{\underline{V}_c}{15Z_c} - \frac{\beta\underline{V}_c}{15Z_c} \quad \text{where } Z_c = \frac{P_c\underline{V}_c}{RT_c}$$

$$f_2(T_c) = 9 P_c(\underline{V}_c-b)^2 - 3.8 RT_c(\underline{V}_c-b)$$

$$f_3(T_c) = 5.4 RT_c(\underline{V}_c-b)^2 - 17 P_c(\underline{V}_c-b)^3$$

$$f_4(T_c) = 12 P_c(\underline{V}_c-b)^4 - 3.4 RT_c(\underline{V}_c-b)^3$$

$$f_5(T_c) = 0.8 RT_c(\underline{V}_c-b)^4 - 3 P_c(\underline{V}_c-b)^5$$

$$C_2 = \frac{[f_2(T_c) + bRT' + \frac{(RT')^2}{P_c}(1-Z_c)](T_B-T_c) + [f_2(T_c) + bRT_B](T_c-T')}{(T_B-T_c) \left( e^{-5.475\frac{T_B}{T_c}} - e^{-5.475\frac{T'}{T_c}} \right) - (T_c-T') \left( e^{-5.475\frac{T_B}{T_c}} - e^{-5.475} \right)}$$

$$B_2 = \frac{-f_2(T_c) - bRT_B - C_2 \left( e^{-5.475\frac{T_B}{T_c}} - e^{-5.475} \right)}{T_B-T_c}$$

$$A_2 = f_2(T_c) - B_2T_c - C_2e^{-5.475}$$

The above formulae are derived by the same procedure as in the original Martin-Hou equation of state<sup>7</sup> which did not have the  $C_5$  term.



In order to derive expressions for the two remaining curvature term constants, the following facts are utilized:

1.  $\frac{d^2P}{dT^2} = 0$  at critical density
2.  $\frac{d^2P}{dT^2} = 0$  at 2.5 x critical density

$$\frac{d^2P}{dT^2} = \frac{C_2}{(\underline{V}-b)^2} + \frac{C_3}{(\underline{V}-b)^3} + \frac{C_5}{(\underline{V}-b)^5} = 0 \text{ at } \underline{V} \text{ and } \frac{V_c}{2.5} .$$

Therefore, eliminating  $C_5$  and solving for  $C_3$  in terms of  $C_2$ ,

$$C_3 = \frac{C_2 [(\underline{V}_c-b)^3 - (\frac{V_c}{2.5}-b)^3]}{[(\frac{V_c}{2.5}-b)^2 - (\underline{V}_c-b)^2]}$$

$$C_5 = -C_2 (\underline{V}_c-b)^3 - C_3 (\underline{V}_c-b)^2$$

or

$$= -C_2 (\frac{V_c}{2.5}-b)^3 - C_3 (\frac{V_c}{2.5}-b)^2$$

$$A_4 = f_4(T_c)$$

$$B_5 = \frac{f_5(T_c) - C_5 e^{-5 \cdot 475}}{T_c}$$

$$B_3 = m(\underline{V}_c-b)^3 - R(\underline{V}_c-b)^2 - B_2(\underline{V}_c-b) - \frac{B_5}{(\underline{V}_c-b)^2}$$

$$A_3 = f_3(T_c) - B_3 T_c - C_3 e^{-5 \cdot 475}$$

The equation of state thus has the following form and constants:

$$P = \frac{RT}{\underline{V}-b} + \frac{A_2 + B_2 T + C_2 e^{-kT/T_c}}{(\underline{V}-b)^2} + \frac{A_3 + B_3 T + C_3 e^{-kT/T_c}}{(\underline{V}-b)^3} + \frac{A_4}{(\underline{V}-b)^4} + \frac{B_5 T + C_5 e^{-kT/T_c}}{(\underline{V}-b)^5} \text{ psia,}$$

where

$$R = 0.088734 \text{ psi-ft}^3/\text{lb-}^\circ\text{R,}$$

$$A_2 = -3.4097271$$

$$\begin{aligned}
 B_2 &= 1.59434848 \times 10^{-3} & T &= \text{°R} \\
 C_2 &= -56.7627671 & V &= \text{ft}^3/\text{lb} \\
 A_3 &= 0.06023944654 \\
 B_3 &= -1.879618431 \times 10^{-5} \\
 C_3 &= 1.31139908 \\
 A_4 &= -5.48737007 \times 10^{-4} \\
 B_5 &= 3.46883400 \times 10^{-9} \\
 C_5 &= -2.54390678 \times 10^{-5} \\
 b &= 0.0065093886 \\
 k &= 5.475 \\
 T_c &= 693.3 \\
 k/T_c &= 7.8970143 \times 10^{-3}
 \end{aligned}$$

A comparison of the experimentally determined PVT data with the equation of state is given in Table III.

TABLE III

COMPARISON OF EQUATION OF STATE WITH  
EXPERIMENTALLY DETERMINED PVT DATA

Density lb/ft <sup>3</sup>	Temp. °R	P abs. psia	P calc. psia	Deviation %	Experimental Investigator
61.633	673.79	737.4	1315.07	43.9	this report Beyond range of validity of equation
	684.16	944.0	1582.40	40.34	
	693.84	1109.4	1846.54	39.92	
	710.06	1424.4	2317.90	38.55	
	721.16	1630.2	2659.31	38.70	
	731.60	1827.9	2993.05	38.93	
	738.75	1958.8	3228.17	39.32	
52.62	698.99	762.1	757.81	-.57	this report
	714.00	947.6	943.21	-.47	
	731.26	1154.3	1170.25	1.36	
	746.08	1353.1	1375.64	1.64	
	762.11	1551.3	1607.36	3.49	
	777.25	1748.2	1834.32	4.69	
	791.69	1935.1	2057.27	5.94	
50.53	696.22	680.0	672.12	-1.17	this report
	716.34	911.7	889.76	-2.47	
	733.98	1123.2	1093.47	-2.72	
	754.10	1357.0	1338.48	-1.38	
	772.30	1560.8	1570.13	.59	
	789.69	1767.2	1799.13	1.77	
	804.00	1942.0	1992.51	2.53	

TABLE III, (Continued)

Density lb/ft <sup>3</sup>	Temp °R	P abs. psia	P calc. psia	Deviation %	Experimental Investigator
49.47	693.57	645.3	629.77	-2.47	this report
	703.72	760.6	730.55	-4.11	
	725.92	1004.7	963.95	-4.23	
	743.34	1199.2	1158.03	-3.55	
	761.39	1410.0	1367.84	-3.08	
	779.63	1626.9	1587.68	-2.47	
	799.30	1861.1	1832.35	-1.57	
45.17	719.27	846.8	822.20	-2.97	this report
	739.63	1035.0	1003.67	-3.12	
	760.84	1230.0	1199.42	-2.55	
	779.77	1424.7	1379.04	-3.31	
	800.17	1636.3	1577.05	-3.76	
	818.40	1798.4	1757.34	-2.34	
	836.09	1980.0	1934.88	-2.33	
44.71	687.86	571.7	556.90	-2.66	this report
	714.34	789.0	775.57	-1.73	
	737.40	1000.3	975.96	-2.49	
	758.86	1199.5	1169.34	-2.58	
	780.15	1400.0	1366.71	-2.44	
	802.24	1612.1	1576.41	-2.26	
	824.18	1827.7	1788.85	-2.17	
43.76	685.11	546.2	535.31	-2.03	this report
	710.31	745.0	735.72	-1.26	
	732.76	937.8	922.42	-1.67	
	756.17	1145.9	1123.89	-1.96	
	778.28	1341.3	1319.50	-1.65	
	799.02	1535.2	1506.93	-1.88	
	821.46	1746.4	1713.35	-1.93	
	840.94	1929.9	1895.13	-1.83	
39.43	714.88	745.9	749.73	.51	this report
	741.61	947.1	942.38	-.50	
	767.15	1136.5	1129.48	-.53	
	793.09	1331.4	1321.99	-.71	
	818.76	1532.0	1514.50	-1.16	
	845.65	1741.0	1717.89	-1.35	
	868.24	1917.6	1889.89	-1.47	

TABLE III, (Continued)

Density lb/ft <sup>3</sup>	Temp °R	P abs. psia	P calc. psia	Deviation %	Experimental Investigator
34.72	698.08	613.8	626.24	1.99	this report
	732.64	829.7	838.27	1.02	
	766.30	1042.0	1044.67	.26	
	796.45	1226.0	1229.49	.28	
	820.17	1371.1	1374.85	.27	
34.64	706.97	684	680.58	-.50	2
	767.13	1027	1048.47	2.05	
	807.81	1284	1296.99	1.00	
	835.06	1453	1463.39	.71	
	846.47	1522	1533.05	.72	
34.38	694.89	600.3	606.56	1.03	this report
	699.08	638.3	632.00	-1.00	
	730.40	610.1	821.95	1.44	
	770.47	1058.5	1064.49	.56	
	797.89	1225.9	1230.23	.35	
32.46	670.09	467.3	463.81	-.75	this report
	672.73	480.3	479.01	-.27	
	676.75	500.3	502.11	.36	
	697.55	608.2	621.10	2.08	
	734.80	823.2	832.16	1.08	
	769.97	1022.7	1029.56	.67	
	806.15	1226.5	1231.20	.38	
	847.10	1450.5	1458.12	.52	
32.41	697.0	612.1	617.93	.94	this report
	709.9	684.7	691.17	.94	
	738.2	841.2	850.85	1.13	
	781.9	1085.6	1095.23	.88	
	818.7	1288.7	1299.46	.83	
	852.1	1477.1	1483.92	.46	
31.73	695.4	616.5	608.49	-1.32	this report
	721.5	750.2	752.84	.35	
	736.1	829.3	832.97	.44	
	756.9	942.4	946.96	.48	
	772.7	1026.5	1032.29	.56	
	794.7	1146.9	1151.20	.37	
	818.7	1280.4	1280.31	-.01	

TABLE III, (Continued)

Density lb/ft <sup>3</sup>	Temp °R	P abs. psia	P calc. psia	Deviation %	Experimental Investigator
20.27	709.8	630	626.57	- .55	this report
	737.2	720	711.59	-1.18	
	757.8	781	774.17	- .88	
	775.6	833	827.46	- .67	
	794.1	885	882.18	- .32	
14.06	676.91	470.3	476.37	1.27	this report
	692.87	512.3	508.26	- .79	
	750.97	612.5	619.92	1.20	
	779.58	681.1	672.93	-1.21	
	805.4	716.3	719.96	.51	
11.936	663.46	416	421.56	1.32	2
	704.09	477	487.18	2.09	
	745.45	535	551.24	2.95	
	786.53	600	612.90	2.10	
	828.29	657	674.12	2.54	
	869.83	715	733.96	2.58	
10.75	682.43	424.0	428.26	.99	this report
	745.62	511.1	514.72	.70	
	814.12	601.5	604.08	.43	
	843.48	639.9	641.47	.24	
6.537	624.22	264.1	263.78	- .13	this report
	627.88	266.1	266.71	.23	
	659.14	298.2	291.21	-2.40	
	696.65	312.4	319.64	2.27	
	735.75	344.7	348.42	1.07	
5.293	608.9	219.8	218.29	- .69	3
	635.0	236.7	234.42	- .97	
	659.8	251.2	249.36	- .74	
	680.0	262.8	261.29	- .58	
	699.8	273.9	272.81	- .40	
5.187	600.14	211.6	209.78	- .87	2
	628.13	227.3	226.81	- .22	
	655.0	243.3	242.68	- .26	
	683.07	256.5	258.87	.92	
	707.89	273.3	272.93	- .14	
	734.87	288.9	287.97	- .32	
	766.82	304	305.53	.50	

TABLE III (Continued)

Density lb/ft <sup>3</sup>	Temp. °R	P abs. psia	P calc. psia	Deviation %	Experimental Investigator
4.756	612.7	204.8	204.08	- .35	3
	614.6	205.7	205.12	- .28	
	641.6	220.2	219.67	- .24	
	669.7	235.2	234.44	- .32	
	688.8	245.3	244.31	- .41	
4.528	595.7	188.5	187.81	- .37	3
	625.1	203.7	203.01	- .34	
	639.8	210.5	210.45	- .02	
	654.8	218.4	217.94	- .21	
	678.0	229.5	229.35	- .07	
	700.3	240.6	240.16	- .18	
	718.7	249.8	248.97	- .33	
3.770	590.7	164.8	161.15	-2.26	3
	671.7	197.6	194.21	-1.75	
3.337	588.9	149.2	145.56	-2.50	3
	671.7	177.7	174.89	-1.61	
3.170	570.86	132.8	133.33	.40	this report
	609.76	145.8	146.73	.63	
	663.49	162.8	164.57	1.08	
	717.42	180.3	181.93	.90	
	764.04	195.3	196.66	.69	
3.00	558.25	122.5	123.34	.68	this report
	572.52	127.2	128.06	.67	
	622.06	142.0	143.97	1.37	
	673.50	158.1	159.88	1.11	
	715.98	169.9	172.72	1.63	
	766.92	185.4	187.86	1.31	
2.891	566.45	121.8	122.32	.43	this report
	577.69	124.9	125.86	.76	
	616.28	136.4	137.72	.96	
	658.20	148.5	150.24	1.16	
	735.20	170.5	172.56	1.19	

TABLE III (Continued)

Density lb/ft <sup>3</sup>	Temp. °R	P abs. psia	P calc. psia	Deviation %	Experimental Investigator
2.821	587.1	129.2	126.17	-2.40	3
	669.9	153.6	150.37	-2.15	
2.361	587.1	110.3	108.37	-1.78	3
	669.9	130.2	128.16	-1.59	
1.804	545.7	79.5	77.79	-2.20	3
	552.9	80.9	79.13	-2.24	
	588.9	87.5	85.72	-2.08	
	669.9	102.2	100.08	-2.12	

Michels<sup>10</sup> has recently measured PVT properties of "Freon-12." The results of his work are compared below with the values calculated from the equation of state used in this report.

COMPARISON OF EQUATION OF STATE WITH EXPERIMENTAL  
DATA OF MICHELS FOR "FREON-12", DICHLORODIFLUOROMETHANE

Volume ft <sup>3</sup> /lb	Temp °R	P <sub>Michels</sub>	P <sub>eqn of state</sub>	Deviation %
.440581	581.67	103.83586	103.433	-.39
	626.67	114.07666	113.866	-.28
	671.67	124.137059	124.040	-.08
	716.67	134.0720377	133.895	-.13
	761.67	143.910541	143.914	+.002
	692.4636	128.737944	128.677	-.05
.342716	581.67	128.690974	128.080	-.47
	626.67	142.2988822	141.985	-.22
	671.67	155.6004512	155.466	-.09
	716.67	168.6998611	168.650	-.03
	761.67	181.6405203	181.627	-.007
	692.4636	161.65902128	161.589	-.04
.280690	581.67	151.3684367	150.526	-.56
	626.67	168.5452009	168.095	-.27
	671.67	185.2343589	185.039	-.11
	716.67	201.6055128	201.544	-.03
	761.67	217.7782926	217.741	-.02
	692.4636	192.8179995	192.711	-.06

Volume ft <sup>3</sup> /lb	Temp °R	P Michels	P eqn of state	Deviation %
.236055	626.67	194.0389929	193.440	-.31
	671.67	214.4510717	214.182	-.13
	716.67	234.4075881	234.310	-.04
	761.67	254.0615965	254.007	-.02
	692.4636	223.7045714	223.546	-.07
.1983965	626.67	221.951149	221.167	-.35
	671.67	247.045396	246.682	-.15
	716.67	271.471206	271.336	-.05
	761.67	295.477100	295.388	-.03
	692.4636	258.391689	258.163	-.09
.1715460	626.67	246.720504	245.780	-.38
	671.67	276.696448	276.224	-.17
	716.67	305.733321	305.530	-.07
	761.67	334.130931	334.040	-.02
	692.4636	290.180419	289.884	-.10
.1463545	626.67	274.631964	274.694	+.02
	671.67	311.173274	312.066	+.29
	716.67	346.364106	347.882	+.44
	761.67	380.701089	382.606	+.50
	692.4636	327.544548	328.777	<u>+.38</u>
Average Deviation				17

6. CHANGES OF ENTHALPY AND ENTROPY USING THE IDEAL GAS HEAT CAPACITY AND THE MARTIN-HOU EQUATION OF STATE WITH C<sub>5</sub> TERM

A. Equation of state:

$$P = \frac{RT}{(V-b)} + \frac{(A_2+B_2T+C_2e^{-KT})}{(V-b)^2} + \frac{(A_3+B_3T+C_3e^{-KT})}{(V-b)^3} + \frac{A_4}{(V-b)^4} + \frac{(B_5T+C_5e^{-KT})}{(V-b)^5} \quad (1)$$

where  $K = \frac{5.475}{T_c} = \frac{k}{T_c}$  .



Derivative with respect to temperature:

$$\begin{aligned} (dP/dT)_{\underline{V}} = & R/(\underline{V}-b) + B_2/(\underline{V}-b)^2 + B_3/(\underline{V}-b)^3 + B_5/(\underline{V}-b)^5 \\ & - [C_2/(\underline{V}-b)^2 + C_3/(\underline{V}-b)^3 + C_5/(\underline{V}-b)^5] Ke^{-KT} \end{aligned} \quad (2)$$

B. Change of enthalpy:

$$d\underline{H} = C_p dT_p + [\underline{V}-T(d\underline{V}/dT)_p] dP_T \quad (3)$$

But

$$\underline{V}dP_T = d(P\underline{V})_T - Pd\underline{V}_T \quad (4)$$

and

$$-(d\underline{V}/dT)_p dP_T = (dP/dT)_{\underline{V}} d\underline{V}_T \quad (5)$$

Putting 4 and 5 into 3,

$$d\underline{H} = C_p dT_p + d(P\underline{V})_T - Pd\underline{V}_T + T(dP/dT)_{\underline{V}} d\underline{V}_T \quad (6)$$

Integrating between  $T^\circ$  at 0 pressure and any given  $T$  and  $P$  or  $\underline{V}$ , where  $\underline{H}^\circ$  is the enthalpy at  $T_0$  and 0 pressure.

$$\underline{H}-\underline{H}^\circ = \int_{T^\circ}^T C_p^\circ dT + [(P\underline{V})_T]_{\underline{V}=\infty}^{\underline{V}} + \int_{\underline{V}=\infty}^{\underline{V}} [T(dP/dT)_{\underline{V}-P}] d\underline{V}_T \quad (7)$$

Substituting 1 and 2 into 7,

$$\begin{aligned} \underline{H}-\underline{H}^\circ = & \int_{T^\circ}^T C_p^\circ dT + [(P\underline{V})_T]_{\underline{V}=\infty}^{\underline{V}} - \int_{\underline{V}=\infty}^{\underline{V}} \frac{A_2 + (1+KT)C_2 e^{-KT}}{(\underline{V}-b)^2} d\underline{V}_T \\ & - \int_{\underline{V}=\infty}^{\underline{V}} \frac{A_3 + (1+KT)C_3 e^{-KT}}{(\underline{V}-b)^3} d\underline{V}_T - \int_{\underline{V}=\infty}^{\underline{V}} \frac{A_4}{(\underline{V}-b)} d\underline{V}_T \\ & - \int_{\underline{V}=\infty}^{\underline{V}} \frac{(1+KT)C_5 e^{-KT}}{(\underline{V}-b)^5} d\underline{V}_T \end{aligned} \quad (8)$$

Integrating;

$$\begin{aligned} \underline{H} - \underline{H}^\circ = & \int_{T^\circ}^T C_p^\circ dT + [(PV)_{\underline{T}}]_{\underline{V}=\infty}^{\underline{V}} + \left[ \frac{A_2 + (1+KT)C_2 e^{-KT}}{(\underline{V}-b)} + \frac{A_3 + (1+KT)C_3 e^{-KT}}{2(\underline{V}-b)^2} \right]_{\underline{V}=\infty}^{\underline{V}} \\ & + \left[ \frac{A_4}{3(\underline{V}-b)^3} + \frac{(1+KT)C_5 e^{-KT}}{4(\underline{V}-b)^4} \right]_{\underline{V}=\infty}^{\underline{V}}, \end{aligned} \quad (9)$$

or

$$\begin{aligned} \underline{H} - \underline{H}^\circ = & \int_{T^\circ}^T C_p^\circ dT + (PV)_{\underline{T}} - RT + \frac{A_2 + (1+KT)C_2 e^{-KT}}{(\underline{V}-b)} + \frac{A_3 + (1+KT)C_3 e^{-KT}}{2(\underline{V}-b)^2} \\ & + \frac{A_4}{3(\underline{V}-b)^3} + \frac{(1+KT)C_5 e^{-KT}}{4(\underline{V}-b)^4}. \end{aligned} \quad (10)$$

$$\Delta \underline{H} = \underline{H}_2 - \underline{H}_1 = (\underline{H}_2 - \underline{H}^\circ) - (\underline{H}_1 - \underline{H}^\circ). \quad (11)$$

Substituting 10 into 11,

$$\begin{aligned} \Delta H = & \int_{T^\circ}^{T_2} C_p dT + (PV)_{T_2} - RT_2 + \frac{A_2 + (1+KT_2)C_2 e^{-KT_2}}{(\underline{V}_2 - b)} \\ & + \frac{A_3 + (1+KT_2)C_3 e^{-KT_2}}{2(\underline{V}_2 - b)^2} + \frac{A_4}{3(\underline{V}_2 - b)^3} + \frac{(1+KT_2)C_5 e^{-KT_2}}{4(\underline{V}_2 - b)^4} \\ & - \int_{T^\circ}^{T_1} C_p dT - (PV)_{T_1} + RT_1 - \frac{A_2 + (1+KT_1)C_2 e^{-KT_1}}{(\underline{V}_1 - b)} \end{aligned} \quad (12)$$

$$- \frac{A_3 + (1+KT_1)C_3 e^{-KT_1}}{2(\underline{V}_1 - b)^2} - \frac{A_4}{3(\underline{V}_1 - b)^3} - \frac{(1+KT_1)C_5 e^{-KT_1}}{4(\underline{V}_1 - b)^4}$$

$$\begin{aligned} \Delta H = & \int_{T_1}^{T_2} C_p^\circ dT - R(T_2 - T_1) + \left[ (PV) + \frac{A_2 + (1+KT)C_2 e^{-KT}}{(\underline{V}-b)} + \frac{A_3 + (1+KT)C_3 e^{-KT}}{2(\underline{V}-b)^2} \right. \\ & \left. + \frac{A_4}{3(\underline{V}-b)^3} + \frac{(1+KT)C_5 e^{-KT}}{4(\underline{V}-b)^4} \right]_{\underline{V}_1, T_1}^{\underline{V}_2, T_2}. \end{aligned} \quad (13)$$

Since  $C_p^\circ = C_v^\circ + R$ ,

$$\Delta H = \int_{T_1}^{T_2} C_v^\circ dT + \left[ \frac{PV}{(V-b)} + \frac{A_2 + (1+KT)C_2 e^{-KT}}{(V-b)} + \frac{A_3 + (1+KT)C_3 e^{-KT}}{2(V-b)^2} + \frac{A_4}{3(V-b)^3} + \frac{(1+KT)C_5 e^{-KT}}{4(V-b)^4} \right]_{V_1, T_1}^{V_2, T_2} \quad (14)$$

C. Change of entropy:

With  $\underline{S}$  as a function of  $\underline{V}$  and  $T$ :

$$d\underline{S} = (d\underline{S}/dT)_{\underline{V}} dT + (d\underline{S}/d\underline{V})_{\underline{T}} d\underline{V} \quad (15)$$

Since

$$C_v = T(d\underline{S}/dT)_{\underline{V}} \text{ and } (d\underline{S}/d\underline{V})_{\underline{T}} = (dP/dT)_{\underline{V}}, \quad (16)$$

$$d\underline{S} = C_v dT/T_{\underline{V}} + (dP/dT)_{\underline{V}} d\underline{V}_{\underline{T}}$$

Integrating between  $T^*$  at a low pressure  $P^*$  where volume is  $\underline{V}^*$ , and any given  $T$  and  $P$  or  $\underline{V}$  where  $\underline{S}^*$  is the entropy in this ideal gas state, and using 2,

$$\underline{S} - \underline{S}^* = \int_{T^*}^T C_v^\circ \frac{dT}{T} + \int_{\underline{V}^*}^{\underline{V}} \left[ \frac{R}{(\underline{V}-b)} + \frac{B_2 - C_2 Ke^{-KT}}{(\underline{V}-b)^2} + \frac{B_3 - C_3 Ke^{-KT}}{(\underline{V}-b)^3} + \frac{B_5 - C_5 Ke^{-KT}}{(\underline{V}-b)^5} \right] d\underline{V}_{\underline{T}} \quad (17)$$

or

$$\underline{S} - \underline{S}^* = \int_{T^*}^T C_v^\circ \frac{dT}{T} + \left[ R \ln (V-b) - \frac{B_2}{(\underline{V}-b)} - \frac{B_3}{2(\underline{V}-b)^2} - \frac{B_5}{4(\underline{V}-b)^4} + \left( \frac{C_2}{(\underline{V}-b)} + \frac{C_3}{2(\underline{V}-b)^2} + \frac{C_5}{4(\underline{V}-b)^4} \right) Ke^{-KT} \right]_{\underline{V}^*}^{\underline{V}} \quad (18)$$

and

$$\Delta \underline{S} = (\underline{S}_2 - \underline{S}^*) - (\underline{S}_1 - \underline{S}^*) \quad (19)$$

Putting 18 into 19,

$$\begin{aligned}
 \Delta \underline{S} = & \int_{T^*}^{T_2} C_V^\circ \frac{dT}{T} + \left[ R \ln (\underline{V}-b) - \frac{B_2}{(\underline{V}-b)} - \frac{B_3}{2(\underline{V}-b)^2} - \frac{B_5}{4(\underline{V}-b)^4} \right. \\
 & + \left. \left( \frac{C_2}{(\underline{V}-b)} + \frac{C_3}{2(\underline{V}-b)^2} + \frac{C_5}{4(\underline{V}-b)^4} \right) Ke^{-KT} \right]_{\underline{V}^*}^{\underline{V}_2} - \int_{T^*}^{T_1} C_V^\circ \frac{dT}{T} \\
 & - \left[ R \ln (\underline{V}-b) - \frac{B_2}{(\underline{V}-b)} - \frac{B_3}{2(\underline{V}-b)^2} - \frac{B_5}{4(\underline{V}-b)^4} \right. \\
 & + \left. \left( \frac{C_2}{(\underline{V}-b)} + \frac{C_3}{2(\underline{V}-b)^2} + \frac{C_5}{4(\underline{V}-b)^4} \right) Ke^{-KT} \right]_{\underline{V}^*}^{\underline{V}_1} .
 \end{aligned} \tag{20}$$

Since  $\underline{V}^*$  is very large,

$$\begin{aligned}
 \Delta \underline{S} = & \int_{T_1}^{T_2} C_V^\circ \frac{dT}{T} + \left[ R \ln (\underline{V}-b) - \frac{B_2}{(\underline{V}-b)} - \frac{B_3}{2(\underline{V}-b)^2} - \frac{B_5}{4(\underline{V}-b)^4} \right. \\
 & + \left. \left( \frac{C_2}{(\underline{V}-b)} + \frac{C_3}{2(\underline{V}-b)^2} + \frac{C_5}{4(\underline{V}-b)^4} \right) Ke^{-KT} \right]_{\underline{V}_1, T_1}^{\underline{V}_2, T_2} .
 \end{aligned} \tag{21}$$

## 7. VAPOR PRESSURE

Three different vapor pressure equations are given below. The first is a four-constant equation of the form

$$\log P = A + \frac{B}{T} + C \log T + DT$$

reported in a private communication.<sup>4</sup> In an effort to obtain a better representation, the data of several investigators were fitted by the method of least squares to a five-constant equation of the form

$$\log P = A + \frac{B}{T} + \frac{C}{T^2} + DT + ET^2 .$$

Subsequent calculations, which were done to check the thermodynamic consistency of the vapor pressure equation with the liquid and vapor heat capacities (see Section 8), have shown that the presence of the  $C/T^2$  term in the equation causes relatively poor checks at low temperatures.

A four-constant equation of the same form as the first was fitted to the data. This equation reproduced the data very well and also provided the best check with the heat capacities. It is recommended for use in the computation of tables of thermodynamic properties of "Freon-12."

(1) Previously reported Equation (4)

$$\log P = 40.1941 - \frac{3446.029}{T} - 12.59294 \log T + 0.00480348 T$$

(2) Five-constant equation

$$\log P = 3.712389 + 1.0390177 \times 10^{-2} T - 1.31524 \times 10^{-11} T^2 - \frac{863.6109}{T} - \frac{197644.4}{T^2}$$

(3) Equation developed in this report (recommended for tables)

$$\log P = 39.883817 - \frac{3436.6322}{T} - 12.471522 \log T + 0.0047304424 T$$

P = psia

T = °R

TABLE IV

VAPOR PRESSURE SUMMARY AND COMPARISON WITH DATA

Temp °R	P <sub>obs</sub>	P <sub>calc</sub> (1)	Dev. %	P <sub>calc</sub> (2)	Dev. %	P <sub>calc</sub> (3)	Dev. %	Experimental Investigator
310.73	0.1622	.16224	-.02	0.1618	.25	.16219	.01	this report
350.96	$\left. \begin{matrix} 1.0200 \\ 1.0204 \end{matrix} \right\}$	1.02044	-.02	1.0275	-.71	1.0202*	.00	$\left. \begin{matrix} \text{this report} \\ 6 \end{matrix} \right\}$
401.70	5.6884	5.679	.16	5.689	-.01	5.6780*	.18	5
455.70	21.894	21.90	-.03	21.83	.29	21.891	.01	5
491.70	44.76	44.787	-.06	44.60	.36	44.760*	.00	11
545.70	107.9	108.2	-.28	107.92	-.02	108.04	-.13	5
569.78	151.8	151.556	.16	151.4	.26	151.27	.35	13
622.88	290.4	291.013	-.21	290.0	-.17	290.08	.11	13
635.70	331.3	335.5	-1.25	335.1	-1.13	334.26	-.88	5
688.21	573.1	572.029	.19	569.3	.67	568.95	.73	this report
693.3	critical	600.25	--	596.9	--	596.9*	--	--

\* Equation fitted through this value

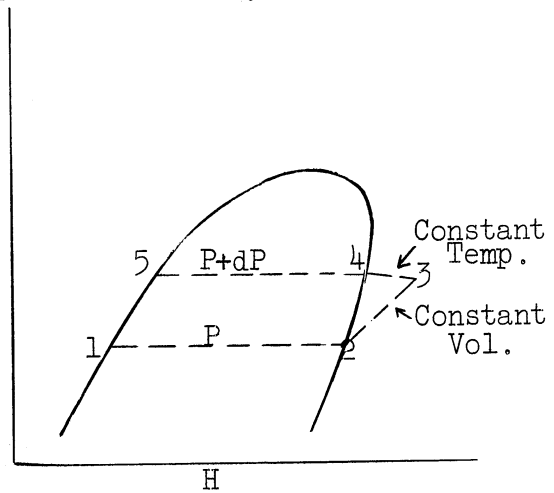
Subsequent to the work of this report, Michels<sup>10</sup> presented some vapor-pressure data. The agreement of the recommended vapor-pressure equation is indeed good, as shown in Table IVA.

TABLE IVA

Temp °R	P <sub>obs</sub> (atm)	P <sub>calc</sub> (3)	Dev. %	P <sub>calc</sub> (1)	Dev. %
545.602	7.328	7.3410	+0.177%	7.3510	+0.313%
580.867	11.873	11.9055	+0.274%	11.9304	+0.481%

8. THE THERMODYNAMIC CONSISTENCY OF THE VAPOR-PRESSURE EQUATION AND THE LIQUID AND GAS HEAT CAPACITIES

Consider an infinitesimal cycle as shown in the diagram here. The enthalpy changes along the five steps permit comparison of the saturated-liquid heat capacity and the ideal gas heat capacity through the vapor-pressure equation. If these heat capacities are reliable, the cycle permits checking of the vapor-pressure equation in the following manner:



From 1 to 2,

$$1) \quad d\underline{H} = (\Delta\underline{H}_{\text{vap}})_T ;$$

from 2 to 3,

$$2) \quad d\underline{H} = C_{\text{vd}}dT + \underline{V} \left( \frac{dP}{dT} \right)_{\underline{V}} dT;$$

from 3 to 4,

$$3) \quad d\underline{H} = T \left( \frac{dP}{dT} \right)_{\underline{V}} + \underline{V}dP = \left[ T \left( \frac{dP}{dT} \right)_{\underline{V}} + \underline{V} \left( \frac{dP}{d\underline{V}} \right)_T \right] d\underline{V};$$

from 4 to 5,

$$4) \quad d\underline{H} = (-\Delta\underline{H}_{\text{vap}})_{T+dT} ;$$

from 5 to 1,

$$5) \quad d\underline{H} = -C_s^l dT - \underline{V}^l \left( \frac{dP}{dT} \right)_s dT .$$

Summing Equations 1 through 5 and solving for  $C_V$ ,

$$6) \quad C_V = C_s^l + \underline{V}^l \left( \frac{dP}{dT} \right)_s + \frac{d(\Delta H)_{\text{vap}}}{dT} - \underline{V} \left( \frac{dP}{dT} \right)_V \\ - \left[ T \left( \frac{dP}{dT} \right)_V + \underline{V} \left( \frac{dP}{dV} \right)_T \right] \left( \frac{dV}{dT} \right)_s$$

Note: Subscript s refers to saturation conditions.  
Superscript l refers to the liquid state.

Using,

$$\left( \frac{dP}{dT} \right)_s = \frac{\Delta H_{\text{vap}}}{T(\underline{V} - \underline{V}^l)_s}$$

$$(\Delta H)_{\text{vap}} = T(\underline{V} - \underline{V}^l)_s \left( \frac{dP}{dT} \right)_s$$

$$7) \quad \frac{d(\Delta H)_{\text{vap}}}{dT} = (\underline{V} - \underline{V}^l)_s \left( \frac{dP}{dT} \right)_s + T(\underline{V} - \underline{V}^l)_s \left( \frac{d^2P}{dT^2} \right)_s \\ + T \left( \frac{dP}{dT} \right)_s \left[ \left( \frac{dV}{dT} \right)_s - \left( \frac{dV^l}{dT} \right)_s \right]$$

Also,

$$dP = \left( \frac{dP}{dT} \right)_V dT + \left( \frac{dP}{dV} \right)_T dV$$

$$8) \quad \left( \frac{dP}{dT} \right)_s = \left( \frac{dP}{dT} \right)_V + \left( \frac{dP}{dV} \right)_T \left( \frac{dV}{dT} \right)_s$$

$$9) \quad \left( \frac{dV}{dT} \right)_s = \frac{\left( \frac{dP}{dT} \right)_s - \left( \frac{dP}{dT} \right)_V}{\left( \frac{dP}{dV} \right)_T}$$

Substitute 7 into 6:

$$\begin{aligned}
 10) \quad C_V &= C_S^l + \underline{V}^l \left( \frac{dP}{dT} \right)_S + \left( \underline{V}_g - \underline{V}^l \right)_S \left[ \left( \frac{dP}{dT} \right)_S + T \left( \frac{d^2P}{dT^2} \right)_S \right] \\
 &\quad - T \left( \frac{dP}{dT} \right)_S \left( \frac{d\underline{V}^l}{dT} \right) - \underline{V} \left( \frac{dP}{dT} \right)_V \\
 &\quad + \left[ T \left( \frac{dP}{dT} \right)_S - T \left( \frac{dP}{dT} \right)_V - \underline{V} \left( \frac{dP}{d\underline{V}} \right)_T \right] \left( \frac{dP}{dT} \right)_S
 \end{aligned}$$

Substitute 8 into 10:

$$\begin{aligned}
 11) \quad C_V &= C_S^l + \underline{V}^l \left( \frac{dP}{dT} \right)_S + (\underline{V} - \underline{V}^l)_S \left[ \left( \frac{dP}{dT} \right)_S + T \left( \frac{d^2P}{dT^2} \right)_S \right] \\
 &\quad - T \left( \frac{dP}{dT} \right)_S \left( \frac{d\underline{V}^l}{dT} \right) - \underline{V} \left( \frac{dP}{dT} \right)_S + T \left[ \left( \frac{dP}{dT} \right)_S - \left( \frac{dP}{dT} \right)_V \right] \left( \frac{d\underline{V}}{dT} \right)_S ;
 \end{aligned}$$

Simplifying,

$$\begin{aligned}
 12) \quad C_V &= C_S^l + (\underline{V} - \underline{V}^l) T \left( \frac{d^2P}{dT^2} \right)_S - T \left( \frac{dP}{dT} \right)_S \left( \frac{d\underline{V}^l}{dT} \right)_S \\
 &\quad + T \left[ \left( \frac{dP}{dT} \right)_S - \left( \frac{dP}{dT} \right)_V \right] \left( \frac{d\underline{V}}{dT} \right)_S ,
 \end{aligned}$$

$$\underline{V}^l = \frac{1}{d^l}$$

$$13) \quad \frac{d\underline{V}^l}{dT} = - \frac{1}{d^{l^2}} \frac{d(d^l)}{dT}$$

Thus equations 9, 12, and 13 determine  $C_V$  as a function of previously given equations and their derivatives.

$C_V$  is related to  $C_V^\circ$  (the ideal gas heat capacity) by the following expression:

$$14) \quad C_V^\circ = C_V + \left( \frac{k}{T_c} \right)^2 T e^{-\frac{KT}{T_c}} \left[ \frac{C_2}{\underline{V}-b} + \frac{C_3}{(\underline{V}-b)^2} \right] (.185052)$$



The conversion factor (.185052) is used when  $C_V$  and  $C_V^\circ$  are expressed in Btu/lb $^\circ$ R. The vapor pressure equation, the equation of state, and the liquid and vapor heat capacities are checked for consistency by comparing the calculated ideal gas heat capacity ( $C_V^\circ$ ) with those reported by Masi.<sup>8</sup> Table V presents these comparisons by use of the three vapor-pressure equations.

The presence of the second derivative of the vapor-pressure equation in the check makes the test quite sensitive. Each of the three vapor-pressure equations fit the vapor-pressure data well; the main influence on the cyclical check appears to be the form of the vapor-pressure equation. At higher temperatures the comparisons are similar for the three equations. However, at low temperatures the second equation predicted large deviations, apparently because of the presence of the  $1/T^2$  term, which becomes very important at low temperatures. This was the major factor in the decision to use the third vapor-pressure equation, which was recommended in Section 7.

TABLE V

$$(1) \log P = 40.1941 - \frac{3446.029}{T} - 12.59294 \log T + 0.00480348 T$$

$$(2) \log P = 3.712388 + 0.001039018 T - 1.31524 \times 10^{-11} T^2 - \frac{863.610928}{T} - \frac{197644.385}{T^2}$$

$$(3) \log P = 39.883817 - \frac{3436.6322}{T} - 12.471522 \log T + 0.0047304424 T$$

$$C_V^\circ = 0.00807939 + 3.32442 \times 10^{-4} T - 2.412299 \times 10^{-7} T^2 + 6.719186 \times 10^{-11} T^3$$

Temp °R	$C_V^\circ$ (Exp.) Btu/lb °R	$C_V^\circ$ calc(1) Btu/lb °R	Dev. %	$C_V^\circ$ calc(2) Btu/lb °R	Dev. %	$C_V^\circ$ calc(3) Btu/lb °R	Dev. %
540	.12792	.13578	5.79	.137	6.63	.1354	5.52
450	.115031	.11806	2.56	.1227	6.25	.11730	1.93
400	.10683	.10492	-1.82	.1046	-2.13	-	-
360	.09970	.09437	-5.65	.0835	-16.2	.09440	-5.61
310	.09005	-	-	.0430	-52.2	.07916	-13.76

9. THE VARIATION OF HEAT CAPACITY ( $C_p$ ) WITH PRESSURE

The variation of heat capacity with pressure can be calculated from the equation of state by means of the relationship

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

This provides a check on the equation of state. Masi<sup>8</sup> measured the heat capacity of "Freon-12" at low pressures. Since the second derivative in the above expression is difficult to evaluate, it has for convenience been evaluated here in the limit as pressure approaches zero. This also corresponds to the low pressures of the observed values.

To obtain the variation of  $C_p$  with pressure, begin with

$$\left(\frac{dC_p}{dP}\right)_T = -T \left(\frac{d^2 V}{dT^2}\right)_P$$

Now

$$\left(\frac{dV}{dT}\right)_P = -\left(\frac{dP}{dT}\right)_V / \left(\frac{dP}{dV}\right)_T$$

and

$$\left[\frac{d\left(\frac{dV}{dT}\right)_P}{dT}\right]_P = \left(\frac{d^2 V}{dT^2}\right)_P = \left(\frac{d\left(\frac{dV}{dT}\right)_P}{dT}\right)_V + \left(\frac{d\left(\frac{dV}{dT}\right)_P}{dV}\right)_T \left(\frac{dV}{dT}\right)_P$$

Therefore,

$$\begin{aligned} \left(\frac{d^2 V}{dT^2}\right)_P &= \frac{-\left(\frac{dP}{dV}\right)_T \left(\frac{d^2 P}{dT^2}\right)_V + \left(\frac{dP}{dT}\right)_V \left(\frac{d^2 P}{dVdT}\right)}{\left(\frac{dP}{dV}\right)_T^2} \\ &+ \frac{\left(\frac{dP}{dV}\right)_T \left(\frac{d^2 P}{dT dV}\right) - \left(\frac{dP}{dT}\right)_V \left(\frac{d^2 P}{dV^2}\right)}{\left(\frac{dP}{dV}\right)_T^2} \left[ \begin{array}{l} \left(\frac{dP}{dT}\right)_V \\ \left(\frac{dP}{dV}\right)_T \end{array} \right] \\ &= \frac{\left(\frac{dP}{dV}\right)_T^2 \left(\frac{d^2 P}{dT^2}\right)_V - 2\left(\frac{dP}{dT}\right)_V \left(\frac{dP}{dV}\right)_T \left(\frac{d^2 P}{dVdT}\right) + \left(\frac{dP}{dT}\right)_V^2 \left(\frac{d^2 P}{dV^2}\right)_T}{\left(\frac{dP}{dV}\right)_T^3} \end{aligned}$$

For the equation of state,

$$P = \frac{RT}{\underline{V}-b} + \frac{F_2(T)}{(\underline{V}-b)^2} + \frac{F_3(T)}{(\underline{V}-b)^4} + \frac{F_5(T)}{(\underline{V}-b)^5},$$

so that

$$\left(\frac{dP}{dT}\right)_{\underline{V}} = \frac{R}{\underline{V}-b} + \frac{F_2'(T)}{(\underline{V}-b)^2} + \frac{F_3'(T)}{(\underline{V}-b)^4} + \frac{F_4'(T)}{(\underline{V}-b)^4} + \frac{F_5'(T)}{(\underline{V}-b)^5}$$

$$\left(\frac{d^2P}{dT^2}\right)_{\underline{V}} = \frac{F_2''(T)}{(\underline{V}-b)^2} + \frac{F_3''(T)}{(\underline{V}-b)^4} + \frac{F_4''(T)}{(\underline{V}-b)^4} + \frac{F_5''(T)}{(\underline{V}-b)^5}$$

$$\left(\frac{dP}{d\underline{V}}\right)_{\underline{T}} = -\frac{RT}{(\underline{V}-b)^2} - \frac{2F_2(T)}{(\underline{V}-b)^3} - \frac{3F_3(T)}{(\underline{V}-b)^4} - \frac{4F_4(T)}{(\underline{V}-b)^5} - \frac{5F_5(T)}{(\underline{V}-b)^6}$$

$$\left(\frac{d^2P}{d\underline{V}^2}\right)_{\underline{T}} = \frac{2RT}{(\underline{V}-b)^3} + \frac{6F_2(T)}{(\underline{V}-b)^4} + \frac{12F_3(T)}{(\underline{V}-b)^5} + \frac{20F_4(T)}{(\underline{V}-b)^6} + \frac{30F_5(T)}{(\underline{V}-b)^7}$$

$$\left(\frac{d^2P}{d\underline{V}dT}\right) = -\frac{R}{(\underline{V}-b)^2} - \frac{2F_2'(T)}{(\underline{V}-b)^3} - \frac{3F_3'(T)}{(\underline{V}-b)^4} - \frac{4F_4'(T)}{(\underline{V}-b)^5} - \frac{5F_5'(T)}{(\underline{V}-b)^6}$$

Substitution of these derivatives where required gives

$$\begin{aligned} \left(\frac{d^2\underline{V}}{dT^2}\right)_P &= -\frac{\left[\frac{RT}{(\underline{V}-b)^2} + \frac{2F_2(T)}{(\underline{V}-b)^3} + \dots\right]^2 \left[\frac{F_2''(T)}{(\underline{V}-b)^2} + \frac{F_3''(T)}{(\underline{V}-b)^3} + \dots\right]}{\left[\frac{RT}{(\underline{V}-b)^2} + \frac{2F_2(T)}{(\underline{V}-b)^3} + \dots\right]^3} \\ &- \frac{2\left[\frac{R}{\underline{V}-b} + \frac{F_2'(T)}{(\underline{V}-b)^2} + \dots\right] \left[\frac{RT}{(\underline{V}-b)^2} + \frac{2F_2(T)}{(\underline{V}-b)^3} + \dots\right] \left[\frac{R}{(\underline{V}-b)^2} + \frac{2F_2(T)}{(\underline{V}-b)^3} + \dots\right]}{\left[\frac{RT}{(\underline{V}-b)^2} + \frac{2F_2(T)}{(\underline{V}-b)^3} + \dots\right]^3} \\ &+ \frac{\left[\frac{R}{\underline{V}-b} + \frac{F_2'(T)}{(\underline{V}-b)^2} + \dots\right] \left[\frac{2RT}{(\underline{V}-b)^3} + \frac{6F_2(T)}{(\underline{V}-b)^4} + \dots\right]}{\left[\frac{RT}{(\underline{V}-b)^2} + \frac{2F_2(T)}{(\underline{V}-b)^3} + \dots\right]^3} \end{aligned}$$

The denominator of the above expression is of the order

$$-6 \text{ in } (\underline{V}-b) \text{ as } P \rightarrow 0 \text{ and } \underline{V} \rightarrow \infty$$

Therefore, in the numerator, consider terms of order -5.

$$-2(R)(RT)(R) + (2RT)(R^2) = -2R^3T + 2R^3T = 0$$

Considering terms of order -6 in the numerator,

$$(RT)^2 F_2''(T) - 2 \left\{ R(RT)[2F_2'(T)] + R[2F_2(T)]R \right. \\ \left. + [F_2'(T)](RT)R \right\} + \left\{ R^2[6F_2(T)] + 2[F_2'(T)]R(2RT) \right\},$$

which simplifies to

$$R^2 T^2 F_2''(T) + 2R^2 F_2(T) - 2R^2 T F_2'(T)$$

In the limit as  $P \rightarrow 0$  and  $V \rightarrow \infty$ , all terms of order -7, -8, etc. in (V-b) in both the numerator and denominator approach zero as compared with the terms of order -6.

Therefore,

$$\lim_{\substack{P \rightarrow 0 \\ V \rightarrow \infty}} \left( \frac{d^2 v}{dT^2} \right)_P = \frac{R^2 T^2 F_2''(T) + 2R^2 F_2(T) - 2R^2 T F_2'(T)}{R^3 T^3}$$

$$= \frac{F_2''(T)}{RT} + \frac{2F_2(T)}{RT^3} - \frac{2F_2'(T)}{RT^2}$$

$$\lim_{P \rightarrow 0} \left( \frac{dC_p}{dP} \right)_T = \lim_{P \rightarrow 0} \left[ -T \left( \frac{d^2 v}{dT^2} \right)_P \right] = \frac{2F_2'(T)}{RT} - \frac{F_2''(T)}{R} - \frac{2F_2(T)}{RT^2}$$

$$F_2(T) = A_2 + B_2 T + C_2 e^{-\frac{K T}{T_c}}$$

$$\lim_{P \rightarrow 0} \left( \frac{dC_p}{dP} \right)_T = \frac{2 \left[ B_2 - \frac{K}{T_c} C_2 e^{-\frac{K T}{T_c}} \right]}{RT} - \frac{\left( \frac{K}{T_c} \right)^2 C_2 e^{-\frac{K T}{T_c}}}{R} \\ - \frac{2 \left[ A_2 + B_2 T + C_2 e^{-\frac{K T}{T_c}} \right]}{RT^2}$$

$$= \left( -\frac{2K}{RT_c T} - \frac{K^2}{T_c^2 R} - \frac{2}{RT^2} \right) C_2 e^{-\frac{K T}{T_c}} + \frac{2A_2}{RT^2}$$

Therefore, at low pressure

$$\left(\frac{\partial C_p}{\partial P}\right)_T = - \frac{C_2 e^{-K/T_c}}{R} \left( \frac{2K}{T_c T} + \frac{K^2}{T_c^2} + \frac{2}{T^2} \right) - \frac{2A_2}{RT^2}$$

The change of the ideal gas heat capacity ( $C_p$ ) with pressure, calculated from the equation of state is compared in Table VI with the values reported by Masi.<sup>8</sup>

TABLE VI

VARIATION OF  $C_p$  WITH PRESSURE

Temp °C	Temp °R	$\left(\frac{\partial C_p}{\partial P}\right)_T$ calc.	$\left(\frac{\partial C_p}{\partial P}\right)_T$ obs.	Dev. %
-30	437.7	0.8544	0.633	+35
0	491.7	0.5496	0.430	+27.8
45	572.7	0.2965	0.218	+36
90	653.7	0.1691	0.137	+23.4

The above values are reported in the units of

$$\frac{\text{cal}}{\text{mole } ^\circ\text{K atm}}$$

The deviations which are of the order of 30% may seem large. However, since this is a very sensitive test of the second derivatives of the equation of state, it is not considered too extreme.

#### 10. CONVERSION FACTORS

Since there has been some confusion as to the most acceptable values of certain constants required in thermodynamic calculations, the following values have been taken from publications of the National Bureau of Standards. It is noted that  $R = 10.7315$  is slightly higher than that used in the equation of state but is well within the experimental data.

Gas law constant  $R = 10.7315 \text{ psia ft}^3/\text{°R lb mole}$

C based on chemical  
scale of atomic  
weights

$R = 1.98719 \text{ thermochemical cal/°K gm mole}$

$R = 1.98589 \text{ Btu/°R lb mole}$

$1 \text{ Btu} = 778.156 \text{ ft lb}$

$1 \text{ int. steam cal} = 1.000654 \text{ thermochemical cal}$

$1 \text{ atm} = 14.696 \text{ psia}$

$1 \frac{\text{Btu}}{\text{lb °R}} = 0.185052 \frac{\text{psia-ft}^3}{\text{lb °R}}$

## BIBLIOGRAPHY

1. Aston, J. G., Pennsylvania State College, Final report to E. I. du Pont de Nemours and Company, October, 1950.
2. Benning, A. F., and McHarness, R. C., Jackson Laboratory Report 30-89, No. 11, SN-15954.
3. Buffington, R. M., and Gilkey, W. K., Ind. Eng. Chem., 23, 254, (1931).
4. Eiseman, B. J., Jr., Personal Communication, September, 1955.
5. Gilkey, W. K., Gerard, F. W., and Bixler, M. E., Ind. Eng. Chem. 23, 364, (1931).
6. Markwood, W. H., E. I. du Pont de Nemours and Company, Jackson Laboratory Report 30-89-12, No. 1, SN-17635.
7. Martin, J. J., and Hou, Y. C., Amer. Inst. Chem. Eng. J., Vol. 1, No. 2 (1955).
8. Masi, J. F., J. Amer. Chem. Soc., 74, 4741, (1952).
9. McHarness, R.C., E. I. du Pont de Nemours and Company, Jackson Laboratory Report 4386-83-86.
10. Michels, A., Personal Communication with D. E. Kvalnes, Jackson Laboratory March, 1955.
11. Pennington, W.A., and Reed, W.H., "The Evolution of a New Refrigerant", Modern Refrigeration, May, June, July (1950).
12. Whitney, J. H., E. I. du Pont de Nemours and Company, Jackson Laboratory Notebook 4713-54.
13. Whitney, J. H., E. I. du Pont de Nemours and Company, Jackson Laboratory Notebook 4713-64-65-83-92.

