

Engineering Research Institute
The University of Michigan
Ann Arbor, Michigan

Data and Equations for the Thermodynamic Properties
of "Freon-C318", Perfluorocyclobutane

by

R. M. Kapoor
B. G. Bray
R. G. Reimus
M. L. Salive
R. K. Bhada

and

J. J. Martin
Project Supervisor

Project 1777
E. I. du Pont de Nemours and Company
Wilmington, Delaware
August, 1956

TABLE OF CONTENTS

	<u>Page</u>
OBJECTIVE	iii
LIST OF TABLES	iv
NOMENCLATURE	v
SUMMARY	vii
I. INTRODUCTION	1
II. LITERATURE SURVEY	2
III. EXPERIMENTAL WORK	3
IV. RESULTS	4
V. PROCEDURE FOR CALCULATING TABLES OF THERMO- DYNAMIC PROPERTIES	11
VI. MARTIN-HOU EQUATION OF STATE WITH A_5 TERM	21
VII. BIBLIOGRAPHY	26

OBJECTIVE

The purpose of this project is to develop the information necessary for calculating tables of thermodynamic properties of "Freon" refrigerants. The present report is devoted to the work done on "Freon-C318", perfluorocyclobutane.

LIST OF TABLES

<u>Table</u>		<u>Page</u>
I	SUMMARY OF AVAILABLE DATA	1a
II	COMPARISON OF VAPOR PRESSURE EQUATION WITH THE EXPERIMENTAL VAPOR PRESSURE DATA	5
III	COMPARISON OF SATURATED LIQUID DENSITY EQUATION WITH THE EXPERIMENTAL DATA	7
IV	COMPARISON OF PVT EQUATION WITH EXPERIMENTAL DATA	9
V	FUNDAMENTAL VIBRATION FREQUENCIES OF "FREON-C318"	12
VI	COMPARISON OF HEAT CAPACITY AT ZERO PRESSURE WITH THE EQUATION	14

NOMENCLATURE

A, B, C, D	Constants of vapor pressure equation
A ₂ , B ₂ , C ₂ , A ₃ , B ₃ , C ₃	Constants in equation of state
A ₄ , A ₅ , B ₅ , C ₅	Equation of state
a, b, c, d	Constants of heat capacity equation
b	Characteristic constant of equation of state
C _p	Heat capacity at constant pressure
C _v	Heat capacity at constant volume
d ^l	Saturated liquid density
e	Base of natural logarithm
f ₁ , f ₂ , f ₃ f ₄ , f ₅	Temperature functions of the equation of state
f ₁ (T _c), f ₂ (T _c) f ₃ (T _c), f ₄ (T _c), f ₅ (T _c)	Temperature functions of the equation of state at T=T _c
<u>H</u>	Enthalpy
<u>ΔH^v</u>	Latent heat of vaporization
J	Conversion factor
k	Constant of equation of state
m	Slope of critical isometric on pressure temperature diagram
N, n	Constants used in developing equation of state
P	Pressure
R	Universal gas constant
S	Entropy
<u>ΔS^v</u>	Entropy of vaporization

T	Absolute temperature, °R (°F + 459.69)
T_B	Boyle point temperature
T'	Absolute temperature for which the slope at $P_r=0$ of the isotherm on the compressibility chart equals the slope of line joining the critical point and ($Z=1, P_r=0$)
\underline{V}	Specific volume
Z	Compressibility factor

Subscripts

-	Bar indicates extensive property per unit mass
V	Constant volume
P	Constant pressure
T	Constant temperature
C	The value at critical point
r	Reduced property

Superscripts

g	Property of gas, Eq. \underline{V}^g
l	Property of liquid, Eq. \underline{V}^l
v	Vaporization property, Eq. \underline{H}^v
★	Star indicates zero pressure

SUMMARY

Experimental data on the critical temperature, vapor pressure, saturated liquid density and pressure-volume-temperature behavior of "Freon-C318", perfluorocyclobutane, have been determined. The ranges of these determinations are as follows:

1. Vapor pressure was measured from 419.94°R to 698.85°R. The corresponding pressure range is from 2.7933 psia to 401.4 psia.
2. The saturated liquid density measurements were made from 473.04°R to 697.27°R. The equivalent liquid density range is from 101.66 lbs/ft³ to 57.9 lbs/ft³.
3. The pressure-volume-temperature measurements cover the following ranges:

Pressure from 65.37 psia to 558.90 psia
 Density from 2.429 lbs/ft³ to 60.73 lbs/ft³
 Temperature from 571.32°R to 875.49°R

4. The critical temperature observed by averaging the appearance and disappearance of the meniscus is 699.27°R. The critical pressure estimated from the vapor pressure equation is 401.44 psia. The critical density obtained by the rectilinear diameter method is 38.70 lbs/ft³.
5. The specific heat of the gas at zero pressure was determined from the spectroscopic data reported by the Naval Research Laboratory. The range covered is from 360°R to 1260°R.

All the above data have been fitted by empirical equations. From these, derived equations have been developed to give the changes in thermodynamic properties such as enthalpy and entropy.

I. INTRODUCTION

This report presents the experimental data and empirical equations necessary for the calculation of a table of thermodynamic properties of "Freon-C318", perfluorocyclobutane.

The thermodynamic properties of general interest are pressure, temperature, volume, enthalpy and entropy of saturated liquid and vapor, and the superheated vapor. The minimum experimental data necessary for this purpose are:

1. Critical temperature.
2. Vapor pressure data.
3. Saturated liquid density data.
4. Heat capacity of the gas at zero pressure.

Critical pressure can be estimated from the vapor pressure equation once the critical temperature has been measured. Critical density is obtained by the rectilinear diameter method which employs the liquid density as a function of temperature. Knowing the critical constants and the vapor pressure data, the Martin-Hou equation of state (9) can be used to predict the PVT behavior of the gas. Thus, the PVT measurements are not absolutely essential; however, they serve as a good check for the calculated values from the equation of state.

Experimental data on vapor pressure, saturated liquid density, PVT behavior and the critical temperature for "Freon-C318" were obtained at the University of Michigan and are reported here. The spectroscopic data on "Freon-C318" reported by the Naval Research Laboratory (10) was used to calculate the spectroscopic specific heat data. Empirical equations for vapor pressure, liquid density, PVT behavior and the specific heat of gas at zero pressure have been developed to represent these data with a high order of precision. These equations are in a form ready for use in an electronic digital computer to calculate tables of thermodynamic properties. The thermodynamic relationships involved in these calculations have been developed and an outline of the procedure for calculating the tables has been included.

A survey of the work done on this compound by other investigators has also been included as shown in Table I.

TABLE I

"Freon-C318"

SUMMARY OF AVAILABLE DATA

Property	This Investigation	Others	Investigator and Year
Vapor Pressure	419.94 to 698.85°R	177 to 274°K 1232.5 to 373.16°K	Furukawa(5) 1954 Graham(6) 1945
Critical Temperature	239.58°F	239.5°F	Graham(6) 1945
Liquid Density	473.04 to 697.27°R	25°F to 195°F	Graham(6) 1945
P-V-T Data	65.37 psia to 558.90 psia 2.429 lbs/ft ³ to 60.73 lbs/ft ³ 571.32°R to 875.44°R		
Specific Heat		10° to 90°C 17 to 270°K	Masi(8) 1953

II. LITERATURE SURVEY

The following experimental data and correlations have been reported by various investigators:

1. CRITICAL TEMPERATURE:

The only data reported are by Graham (6). He found the critical temperature to be 239.5°F.

2. VAPOR PRESSURES:

These data are available from two sources:

- (a) Graham (6) reported the results of his measurements from -41.19°F to 212°F. The data have been represented by an equation of the form:

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

- (b) Furakawa et al (5) measured the vapor pressure of "Freon-C318" from 77 to 274°K. They have developed an equation of the form:

$$\log_{10} P = A + \frac{B}{T} + CT + DT^2$$

They claim that this equation represents the data within ± 0.5 mm. of Hg. in most cases.

3. SATURATED LIQUID DENSITY AND PVT BEHAVIOR:

Graham (6) has reported empirical equations based on the preliminary work done on this compound at the du Pont laboratories.

4. SPECTROSCOPIC DATA:

- (a) Edgell (2) measured the Raman and Infrared spectra of his compound in his study of the spatial configuration of cyclo compounds. His results were later used to check the calorimetric measurements of heat capacity made by Lacher (7) at the du Pont laboratories.
- (b) The Naval Research Laboratory, in a report entitled "Spectroscopic Properties of Fluorocarbons and Fluorinated Hydrocarbons" (10), gives the results of measurements of the fundamental vibrational frequencies of perfluorocyclobutane. The calculated heat capacity at zero pressure has also been reported at 5 values of temperature ranging from 268° to 600°K.

5. SPECIFIC HEAT OF GAS:

Specific heat measurements by a calorimetric method have been reported by the following:

- (a) Masi (8) measured the heat capacity of gaseous perfluorocyclobutane with a constant flow calorimeter at three pressures at each of the temperatures 10, 50 and 90°C. He claims an accuracy of 0.1 percent in these measurements. The specific heat of the gas at zero pressure, obtained by extrapolation and believed reliable to 0.15 percent has also been reported.
- (b) Furukawa et al (5) obtained the heat capacity data in an adiabatic calorimeter from 17° to 270°K. They claim an accuracy of about 0.2 percent except in the transition regions of 141.3° and 174.6°K, the anomalous region of 97°K (attributed to glass transformation) and below 50°K.
- (c) Lacher (7) determined the heat capacity of the gas at the du Pont laboratories in a preliminary investigation on this compound.

III. EXPERIMENTAL WORK

The experimental work in this study involved the measurements of vapor pressure, saturated liquid density, critical temperature and pressure-volume-temperature behavior of the gas.

The sample of "Freon-C318", perfluorocyclobutane, was supplied by E. I. du Pont de Nemours and Company. It was a fractionated product which contained no impurities detectable by infrared analysis. The moisture content of the sample was 0.0005 weight percent and an air content in the vapor phase of 0.011 volume percent.

The equipment used and the experimental technique employed were essentially the same as described in the "Freon-23", (trifluoromethane,) report (3).

The vapor pressure measurements were made by the static method. A sample of the perfluorocyclobutane was charged to the system and the vapor pressure exerted by it was measured at intervals of temperature.

The saturated liquid density was measured by the method of Benning and McHarness (1). In this system, the temperature was found at which the saturated liquid had a known density.

The critical temperature measurement was based on the phenomena of disappearance and reappearance of the meniscus

between the vapor and liquid phases. The average of the two temperatures at which the disappearance and reappearance of the meniscus occur was considered to be practically the critical temperature.

The pressure-volume-temperature measurements were carried out as a series of approximately constant volume and hence, constant density runs. The pressures at various temperatures for each run were recorded, making sure that the system was leakproof during the run. For a detailed description of the equipment and the experimental procedure, a reference to the "Freon-23" report is suggested.

IV. RESULTS

The following equations have been developed to represent the experimental data obtained in this investigation:

1. VAPOR PRESSURE

The general form of the equation chosen to represent the vapor pressure data is:

$$\log_{10}P = A + \frac{B}{T} + C \log_{10}T + DT \quad (1)$$

The constants of the equation were obtained by fitting the experimental data by the method of least squares. The constants are:

$$A = 46.8587746$$

$$B = -4,270.76331$$

$$C = -14.573528$$

$$D = +0.00473182$$

The pressure is in lbs/sq.in. and temperature in °R (°F+459.69)

The experimental data and its comparison with the calculated values are shown in Table II on the following page.

2. LIQUID DENSITY EQUATION

The following form of empirical equation was developed in the "Freon-23" report (3) to represent the density of the saturated liquid.

$$d^l = a_0 + a_1 \left(1 - \frac{T}{T_c}\right)^{1/3} + a_2 \left(1 - \frac{T}{T_c}\right)^{2/3} + a_3 \left(1 - \frac{T}{T_c}\right) + a_4 \left(1 - \frac{T}{T_c}\right)^{4/3} \quad (2)$$

At the critical temperature, the equation reduces to the form of $d^l = a_0$; so that a_0 is the critical density. This value was obtained by the rectilinear diameter method.

TABLE II

COMPARISON OF VAPOR PRESSURE EQUATION WITH THE EXPERIMENTAL
VAPOR PRESSURE DATA

VAPOR PRESSURE EQUATION:

$$\log_{10} P = 46.8587746 - \frac{4,270.76331}{T} - 14.573528 \log_{10} T + 0.00473182 T$$

<u>T°R</u>	<u>P_{exp.} lb/sq.in.</u>	<u>P_{calc.} lb/sq.in.</u>	<u>Percent Deviation[†]</u>
419.94	2.7933	2.7976	-0.15
424.69	3.2635	3.2504	+0.40
428.80	3.7081	3.6873	+0.56
437.99	4.8521	4.8433	+0.18
466.13	10.205	10.296	-0.89
479.14	14.024	14.025	-0.07
480.53	14.393	14.549	-1.08
482.17	14.969	15.105	-0.91
498.19	21.391	21.529	-0.64
520.67	34.300	33.894	+1.18
531.55	41.88	41.55	+0.79
531.55	42.14	41.55	+1.40
549.36	57.19	56.86	+0.58
549.70	57.83	57.18	+1.12
571.88	81.74	81.87	-0.16
549.02	113.09	113.72	-0.56
600.59	124.59	124.72	-0.26
619.36	159.46	160.54	-0.68
637.85	201.26	202.67	-0.70
653.18	242.06	243.35	-0.53
669.62	291.46	293.11	-0.57
677.09	317.14	318.17	-0.32
687.98	358.33	357.15	+0.33
696.69	393.03	390.95	+0.53
698.85	402.83	395.55	+1.81

$$^{\dagger}\text{Percent Deviation} = \frac{\text{Exp.} - \text{Cal.}}{\text{Exp.}} \times 100$$

The other constants of this equation were obtained by fitting the equations to four evenly distributed values of temperature and liquid density. The constants thus obtained are:

$$a_0 = 38.70$$

$$a_1 = 70.85831830$$

$$a_2 = 23.60975930$$

$$a_3 = 15.98918211$$

$$a_4 = -8.924385653$$

The liquid density, d^l , is in lbs/ft^3 and the temperature is in $^{\circ}\text{R}$.

The comparison of calculated values with the experimental data is shown in Table III.

3. EQUATION OF STATE

The PVT behavior is represented by the Martin-Hou equation of state (9). This equation has been modified by the addition of an A_5 term, this addition being necessitated in the higher density range (about 1.5 critical density). A full discussion of this is given later. The modified form of the equation is:

$$P = \frac{RT}{(\underline{V}-b)} + \frac{A_2+B_2T+C_2e^{-\frac{kT}{T_c}}}{(\underline{V}-b)^2} + \frac{A_3+B_3T+C_3e^{-\frac{kT}{T_c}}}{(\underline{V}-b)^3} + \frac{A_4}{(\underline{V}-b)^4} + \frac{A_5+B_5T+C_5e^{-\frac{kT}{T_c}}}{(\underline{V}-b)^5} \quad (3)$$

The information numbers used in evaluating the constants of the equation are:

$$T_c = 699.27^{\circ}\text{R}$$

$$V_c = .0258397932 \text{ ft}^3/\text{lb}$$

$$P_c = 401.44 \text{ psia}$$

$$\beta = 3.24$$

$$M = 4.68$$

$$T' = 0.81 T_c$$

$$T_B = 1575^{\circ}\text{R}$$

TABLE III

COMPARISON OF SATURATED LIQUID DENSITY EQUATION
WITH THE EXPERIMENTAL DATA

SATURATED LIQUID DENSITY EQUATION:

$$d^l = 38.70 + 70.85831830 \left(1 - \frac{T}{T_c}\right)^{\frac{1}{3}} + 23.60975930 \left(1 - \frac{T}{T_c}\right)^{\frac{2}{3}} + 15.98981211 \left(1 - \frac{T}{T_c}\right)^{\frac{4}{3}} - 8.924385653 \left(1 - \frac{T}{T_c}\right)^{\frac{4}{3}}$$

<u>T°R</u>	<u>P_{exp.} lb/ft³</u>	<u>P_{calc.} lb/ft³</u>	<u>Percent Deviation[†]</u>
698.67	45.237	45.659	-0.93
★697.27	49.276	49.276	0.00
688.91	57.386	57.732	-0.60
★659.20	70.246	70.246	0.00
650.07	72.962	72.842	+0.16
★583.97	86.484	86.484	0.00
532.15	94.132	94.263	-0.14
★473.04	101.661	101.661	0.00

★Equation fitted to these points

$$†\text{Percent Deviation} = \frac{(d^l)_{\text{exp.}} - (d^l)_{\text{calc.}}}{(d^l)_{\text{exp.}}}$$

$$k = 5.0$$

$$n = 1.7$$

$$N = 17 M$$

The constants of the equation obtained by the method discussed later are:

$$A_2 = -1.782832574$$

$$B_2 = +0.8288016876 \times 10^{-3}$$

$$C_2 = -29.98281801$$

$$A_3 = +2.220141064 \times 10^{-2}$$

$$B_3 = -0.7000454923 \times 10^{-6}$$

$$C_3 = +0.6970502981$$

$$A_4 = -2.49243233 \times 10^{-4}$$

$$A_5 = +1.027671206 \times 10^{-6}$$

$$B_5 = +0.2444029514 \times 10^{-9}$$

$$C_5 = -3.742878007 \times 10^{-5}$$

$$R = 0.0536456979 \text{ (psia) (ft}^3\text{) / (lb) (}^\circ\text{R)}$$

$$k = 5.0$$

$$b = 0.005655630365$$

It will be noticed that the value of k has been changed from 5.475, as suggested in the paper by Martin and Hou (9), to 5.0. This change was made to improve the curvature of the isometrics, and is in keeping with the suggestions in their paper.

TABLE IV

COMPARISON OF CALCULATED PVT DATA WITH
EXPERIMENTAL DATA FOR "FREON-C318"

<u>Density</u> <u>lb/cu.ft.</u>	<u>T°R</u>	<u>P_{exp.} lb/sq.in.</u>	<u>P_{calc.}</u>	<u>Percent</u> <u>Deviation</u>
2.148	572.63	58.4	58.59	-0.325
	641.52	69.2	67.76	+0.21
	711.18	77.2	76.70	+0.65
	785.07	86.5	85.95	+0.64
	862.42	96.7	95.48	+1.26
2.429	571.32	65.37	64.97	+0.612
	645.07	76.35	76.27	+0.105
	710.19	87.95	85.83	+2.41
	781.52	97.47	96.04	+1.47
	851.83	107.70	105.94	+1.634
7.900	651.44	199.5	199.45	-0.03
	698.42	227.7	227.42	+0.123
	768.55	266.7	266.91	-0.0787
	813.03	291.6	291.00	+0.0206
	849.84	312.0	310.55	+0.465
15.03	680.89	313.40	312.02	+0.440
	720.65	365.40	365.43	-0.0082
	761.67	419.00	418.05	+0.227
	809.01	480.50	476.47	+0.839
	820.86	495.50	490.79	+0.951
	875.49	558.90	555.99	+0.521
22.31	694.68	376.0	374.98	+0.271
	728.25	454.5	451.20	+0.726
	769.11	544.0	540.45	+0.653
	820.64	651.3	648.93	+0.364
	864.33	742.0	740.34	+0.224
33.30	699.52	403.9	402.14	+0.436
	738.79	555.4	553.58	+0.328
	776.94	695.4	698.10	-0.388
	825.55	874.4	879.52	-0.586
	852.59	973.4	979.42	-0.618
44.45	707.28	453.0	446.09	+1.525
	749.99	681.0	687.30	-0.925
	782.89	873.4	876.97	-0.409
	816.25	1069.4	1071.95	-0.238
	857.52	1313.4	1316.00	-0.198

TABLE IV
(continued)

<u>Density</u> <u>lb/cu.ft.</u>	<u>T°R</u>	<u>P_{exp.} lb/sq.in.</u>	<u>P_{calc.}</u>	<u>Percent</u> <u>Deviation</u>
50.84	698.80	402.0	402.13	-0.032
	704.49	444.0	440.60	+0.766
	752.14	781.4	774.76	+0.850
	796.81	1111.4	1103.54	+0.707
	838.86	1430.4	1422.97	+0.519
	862.04	1612.4	1602.22	+0.631
55.77	695.95	405.9	398.01	+1.944
	721.19	616.4	610.08	+1.025
	763.76	987.4	985.61	+0.181
	801.60	1338.4	1334.09	+0.322
	861.36	1895.4	1904.62	-0.486
60.73	688.25	373.4	386.89	-3.613
	716.71	668.4	705.33	-5.525
	754.51	1080.4	1143.88	-5.8756
	792.09	1502.9	1593.66	
	831.08	1946.9	2071.39	-6.4216

symmetry species of this assignment is B_{1u} and it was shifted from 613 to 972. This gave a better comparison of the calculated heat capacity with the experimental data reported by Masi (8). The fundamental vibration frequencies generally used to calculate the heat capacity are given in Table V.

Results of calculations of the heat capacity of the gas at zero pressure were also given in the above mentioned report at temperatures ranging from 268°K to 600°K. These results were modified for the change in the fundamental assignment indicated. Additional calculations of heat capacity were made at various values of temperature within the above range to get a good spread of the data. All the results thus obtained are shown in Table VI.

HEAT CAPACITY EQUATION:

The calculated spectroscopic heat capacities were represented by an equation of the form:

$$C_p^* = a + bT + cT^2 + dT^3 \quad (4)$$

The constants of this equation are:

$$a = 6.49044393$$

$$b = 7.399783877 \times 10^{-2}$$

$$c = -3.297575755 \times 10^{-5}$$

$$d = 4.306508915 \times 10^{-9}$$

Here T is in °R and C_p^* is Btu/(lb mole)(°R)

A comparison of the calculated values with the spectroscopic results is shown in Table VI. At three values of temperature given in Table VI, Masi's (8) data obtained by calorimetric measurements were also available. These are shown within parentheses and the deviations have been calculated.

V. PROCEDURE FOR CALCULATING

TABLES OF THERMODYNAMIC PROPERTIES

The calculations of tables of thermodynamic properties, in general, are based on exact thermodynamic relations. The approach to the problem varies with the type of experimental data available. The purpose of this section is to indicate how the empirical equations presented earlier can be utilized to obtain tables of thermodynamic properties. The discussion is presented under two headings:

1. Properties of the saturated liquid and vapor.
2. Properties of superheated vapor.

TABLE V

FUNDAMENTAL VIBRATION FREQUENCIES OF PERFLUOROCYCLOBUTANE

<u>SYMMETRY SPECIES</u>	<u>APPROXIMATE \star^2 CHARACTER</u>	<u>WAVE NUMBER</u>	
		<u>INFRARED (GAS)</u>	<u>RAMAN (GAS)</u>
A _{1g}	CF Stretching		1431.3 cm ⁻¹
A _{1g}	Ring Stretching		699.3
A _{1g}	CF ₂ Deformation		358.2
A _{2u}	CF Stretching	1239	
A _{2u}	CF ₂ Rocking	338	
B _{1g}	CF Stretching		1220
B _{1g}	CF ₂ Wagging		258
B _{2g}	CF Stretching		1008
B _{2g}	CF ₂ Deformation		659.5
B _{2g}	In-plane ring bending		192
E _g	CF Stretching		1285
E _g	CF ₂ Twisting		439
E _g	CF ₂ Twisting		273
E _u	CF Stretching	1340	
E _u	Ring Stretching	962	
E _u	CF ₂ Deformation	569	
E _u	CF ₂ Wagging	(285)	

\star^1 Fundamentals not observed directly are enclosed in parentheses.

\star^2 Only very rough meaning can be attached to the terms used in this column.

TABLE V

(continued)

INACTIVE VIBRATIONS

<u>SYMMETRY SPECIES</u>	<u>APPROXIMATE CHARACTER</u>	<u>CALCULATED VALUE</u>
A _{1u}	CF ₂ Twisting	(173)
A _{2g}	CF ₂ Wagging	(745)
B _{1u}	CF Stretching	(1385)
B _{1u}	CF ₂ Rocking	(972)★ ³
B _{1u}	Out of plane ring bending	(86)
B _{2u}	CF ₂ Twisting	(250)

★³ This assignment has been modified. The original assignment reported is (613).

TABLE VI

COMPARISON OF HEAT CAPACITY AT ZERO PRESSURE

WITH THE EQUATION

HEAT CAPACITY EQUATION

$$C_p^* = 6.490443930 + 7.399783877 \times 10^{-2} T - 3.297575755 \times 10^{-5} T^2 + 4.306508915 \times 10^{-9} T^3 \text{ Btu}/(\text{lb mole})(^\circ\text{R})$$

SPECTROSCOPIC HEAT CAPACITY⁺¹

HEAT CAPACITY EQUATION

<u>T^{°R}</u>	<u>C_p[*]</u>	<u>C_p[*]</u>	<u>Percent Deviation +2</u>
360.00	28.947	29.057	-0.29
432.00	32.651	32.651	0.00
509.69	36.215 (36.19)	36.210	+0.01 (.06)
536.40	37.369	37.360	+0.03
563.40	38.491	38.484	+0.02
581.69	39.224 (39.23)	39.224	0.00 (0.02)
653.69	41.974 (42.01)	41.974	0.00 (0.09)
720.00	44.282	44.282	0.00
900.00	49.493	49.518	-0.05
1080.00	53.387	53.370	+0.03
1260.00	56.272	55.990	+0.50

⁺¹Masi's calorimetric values are given in parentheses

$$^+2 \text{ Percent Deviation} = \frac{(C_p^*)_{\text{Spec.}} - (C_p^*)_{\text{Calc.}}}{(C_p^*)_{\text{Spec.}}} \times 100$$

The general procedure is as follows:

1. Saturation properties:

The properties to be evaluated are:

- (a) Volume of saturated vapor.
- (b) Volume of saturated liquid.
- (c) Enthalpy and entropy of vaporization.
- (d) Enthalpy of saturated vapor and liquid.
- (e) Entropy of saturated vapor and liquid.

Before any calculations of these properties are undertaken, it is necessary to decide on the temperature range available and the intervals of the temperature desired in the tables. The former is limited by the triple point at one end and the critical point at the other. The temperature interval in the intermediate range is mostly a matter of choice depending on the ease of the user, and the extensiveness of the tables desired. Having fixed this, the properties are evaluated as follows:

- (i) Saturation pressure is obtained from the vapor pressure equation (1) by substituting the values of temperature fixed above.
- (ii) The volume of saturated vapor is obtained by substituting the values of pressure and temperature in the equation of state (3).
- (iii) Saturated liquid volume is simply the reciprocal of saturated liquid density which has been represented by an equation as a function of temperature (Eqn. 2).
- (iv) [a] The enthalpy of vaporization is calculated from the Clapeyron equations:

$$\frac{dP}{dT} = \frac{\Delta H^v}{T(\underline{v}^g - \underline{v}^l)J} \quad (5)$$

where \underline{v}^g = volume of vapor (ft³/lb)

\underline{v}^l = volume of liquid (ft³/lb)

J = conversion factor

The vapor pressure equation (1) is differentiated to give

$$\frac{dP}{dT} = e^{[2.302585(A + \frac{B}{T} + DT) + C \ln T]} \times \left[2.302585 \left(\frac{B}{T^2} + D \right) + \frac{C}{T} \right] \quad \dots (1a)$$

[b] The entropy of vaporization is obtained from the following equation:

$$\underline{s}^v = \frac{dP}{dT}(\underline{v}^g - \underline{v}^l)J \quad (5a)$$

(v) [a] The calculations of enthalpy and entropy are based on some datum temperature at which both these properties are zero. This is an arbitrary choice and can be any value whatsoever.

[b] The equations used to calculate the enthalpy of vapor are next developed.

Enthalpy of Vapor

The fundamental relation which expresses the effect of temperature and pressure on enthalpy is:

$$d\underline{H} = C_p dT_p + [\underline{V} - T(d\underline{V}/dT)_p]dP_T \quad (6)$$

$$\text{But } \underline{V}dP_T = d(P\underline{V})_T - Pd\underline{V}_T \quad (7)$$

$$\text{and } -(d\underline{V}/dT)_p dP_T = (dP/dT)_V d\underline{V}_T \quad (8)$$

Substituting (7) and (8) in equation (6), we get

$$d\underline{H} = C_p dT_p + d(P\underline{V})_T - Pd\underline{V}_T + T\left(\frac{dP}{dT}\right)_V d\underline{V}_T \quad (9)$$

Integrating between T at 0 pressure, the datum conditions, and any given T and P or \underline{V} , and substituting the equation of state and its derivative with respect to T in the above equation we have:

$$\underline{H} - \underline{H}_0 = \int_{T_0}^T C_p^* dT + \left[(P\underline{V})_T \right]_{\infty}^{\underline{V}} + \int_{\underline{V}=\infty}^{\underline{V}} \left[\frac{A_2 + C_2 e^{-k\frac{T}{T_c}} \left(1 + k \frac{T}{T_c}\right)}{(\underline{V} - b)^2} - \frac{A_3 + C_3 e^{-k\frac{T}{T_c}} \left(1 + k \frac{T}{T_c}\right)}{(\underline{V} - b)^3} - \frac{A_4}{(\underline{V} - b)^4} - \frac{A_5 + C_5 e^{-k\frac{T}{T_c}} \left(1 + k \frac{T}{T_c}\right)}{(\underline{V} - b)^5} \right] d\underline{V}_T \quad (10)$$

where subscript, o, indicates datum condition.

Integrating:

$$\begin{aligned} \underline{H} - \underline{H}_o = & \int_{T_o}^T C_P^* dT + \left[(PV)_T \right]_{V=\infty}^V + \left[\frac{A_2 + C_2 e^{-k \frac{T}{T_c}} \left(1 + k \frac{T}{T_c} \right)}{(\underline{V} - b)} \right. \\ & + \frac{A_3 + C_3 e^{-k \frac{T}{T_c}} \left(1 + k \frac{T}{T_c} \right)}{2(\underline{V} - b)^2} + \frac{A_4}{3(\underline{V} - b)^3} \\ & \left. + \frac{A_5 + C_5 e^{-k \frac{T}{T_c}} \left(1 + k \frac{T}{T_c} \right)}{4(\underline{V} - b)^4} \right]_{V=\infty}^V \end{aligned} \quad (11)$$

$$\text{Now } \Delta H = \underline{H}_2 - \underline{H}_1 = (\underline{H}_2 - H_o) - (\underline{H}_1 - H_o) \quad \text{and} \quad (12)$$

$$C_P^* = C_V^* + R \quad (13)$$

Substituting equation (11) into (12), combining with (13) and simplifying we get

$$\begin{aligned} \Delta \underline{H} = & \left[C_V^* dT + PV + \frac{A_2 + C_2 e^{-k \frac{T}{T_c}} \left(1 + k \frac{T}{T_c} \right)}{(\underline{V} - b)} \right. \\ & + \frac{A_3 + C_3 e^{-k \frac{T}{T_c}} \left(1 + k \frac{T}{T_c} \right)}{2(\underline{V} - b)^2} + \frac{A_4}{3(\underline{V} - b)^3} \\ & \left. + \frac{A_5 + C_5 e^{-k \frac{T}{T_c}} \left(1 + k \frac{T}{T_c} \right)}{4(\underline{V} - b)^4} \right]_{V_1, T_1}^{V_2, T_2} \end{aligned} \quad (14)$$

Using the references properties as P_1, V_1, T_1 and H_1 , equation (14) will give $\underline{H}_1 - H_{ref}$. Dropping the subscript 2 in order to generalize the properties for any temperature and pressure, we have

$$\begin{aligned}
 \underline{H} = & (a-R)T + \frac{bT^2}{2} + \frac{cT^3}{3} + \frac{dT^4}{4} + P\underline{V} + \frac{A_2+C_2e^{-k\frac{T}{T_c}}\left(1 + k\frac{T}{T_c}\right)}{\underline{V} - b} \\
 & + \frac{A_3C_3e^{-k\frac{T}{T_c}}\left(1 + k\frac{T}{T_c}\right)}{2(\underline{V} - b)^2} + \frac{A_4}{3(\underline{V} - b)^3} \\
 & + \frac{A_5C_5e^{-k\frac{T}{T_c}}\left(1 + k\frac{T}{T_c}\right)}{4(\underline{V} - b)^4} + X
 \end{aligned} \tag{15}$$

$$\begin{aligned}
 \text{where } X = H_{\text{ref}} - & \left[(a - R)T_{\text{ref}} + \frac{1}{2}b T_{\text{ref}}^2 + \frac{1}{3}cT_{\text{ref}}^3 + \frac{1}{4}dT_{\text{ref}}^4 \right. \\
 & + P_{\text{ref}}\underline{V}_{\text{ref}} + \frac{A_2+C_2e^{-k\frac{T_{\text{ref}}}{T_c}}\left(1 + k\frac{T_{\text{ref}}}{T_c}\right)}{(\underline{V}_{\text{ref}} - b)} \\
 & + \frac{A_3+C_3e^{-k\frac{T_{\text{ref}}}{T_c}}\left(1 + k\frac{T_{\text{ref}}}{T_c}\right)}{2(\underline{V}_{\text{ref}} - b)^2} + \frac{A_4}{3(\underline{V}_{\text{ref}} - b)^3} \\
 & \left. + \frac{A_5+C_5e^{-k\frac{T_{\text{ref}}}{T_c}}\left(1 + k\frac{T_{\text{ref}}}{T_c}\right)}{4(\underline{V}_{\text{ref}} - b)^4} \right]
 \end{aligned} \tag{16}$$

Equation (15) is the final form of equation used for calculating the vapor enthalpy. For the given set of constants for the heat capacity equation and the equation of state, values of enthalpy at the temperatures fixed can be thus evaluated by simple substitution of corresponding volume and pressure values.

- (v) [c] The liquid enthalpy is the difference between the enthalpy of vapor and latent heat of vaporizations and can be directly calculated.

Entropy of Vapor

(vi) [a] The equations used to calculate the entropy of vapor are developed as follows:

The fundamental equation for entropy is:

$$d\underline{S} = \underline{C}_V \left(\frac{dT}{T} \right)_{\underline{V}} + \left(\frac{dP}{dT} \right)_{\underline{V}} d\underline{V}_T \quad (17)$$

Integrating the above equation between T at 0 pressure and any given T and P or \underline{V} , we have

$$\begin{aligned} \underline{S} - \underline{S}_0 = & \int_{T_0}^T \underline{C}_V^* \frac{dT}{T} + \int_{\underline{V}^*}^{\underline{V}} \left[\frac{R}{\underline{V} - b} + \frac{B_2 - C_2 \frac{k}{T_c} e^{-\frac{kT}{T_c}}}{(\underline{V} - b)^2} \right. \\ & \left. + \frac{B_3 - C_3 \frac{k}{T_c} e^{-\frac{kT}{T_c}}}{(\underline{V} - b)^3} + \frac{B_5 - C_5 \frac{k}{T_c} e^{-\frac{kT}{T_c}}}{(\underline{V} - b)^5} \right] d\underline{V}_T \quad (18) \end{aligned}$$

$$\begin{aligned} \text{or } \underline{S} - \underline{S}_0 = & \int_{T_0}^T \underline{C}_V^* \frac{dT}{T} + \left[R \ln(\underline{V} - b) - \frac{B_2}{(\underline{V} - b)} - \frac{B_3}{2(\underline{V} - b)^2} \right. \\ & \left. - \frac{B_5}{4(\underline{V} - b)^4} + \frac{C_2}{(\underline{V} - b)} + \frac{C_3}{2(\underline{V} - b)^2} + \frac{C_5}{4(\underline{V} - b)^4} \frac{k}{T_c} e^{-\frac{kT}{T_c}} \right]_{\underline{V}_0}^{\underline{V}} \\ & \dots\dots\dots (19) \end{aligned}$$

$$\text{Also } \Delta \underline{S} = (\underline{S}_2 - \underline{S}_0) - (\underline{S}_1 - \underline{S}_0) \quad (20)$$

Substituting (19) into (20),

$$\begin{aligned} \Delta \underline{S} = & \int_{T_1}^{T_2} \underline{C}_V^* \frac{dT}{T} + \left[R \ln(\underline{V} - b) - \frac{B_2}{(\underline{V} - b)} - \frac{B_3}{2(\underline{V} - b)^2} - \frac{B_5}{4(\underline{V} - b)^4} \right. \\ & \left. + \frac{k}{T_c} e^{-\frac{kT}{T_c}} \frac{C_2}{(\underline{V} - b)} + \frac{C_3}{2(\underline{V} - b)^2} + \frac{C_5}{4(\underline{V} - b)^4} \right]_{\underline{V}_1, T_1}^{\underline{V}_2, T_2} \quad (21) \end{aligned}$$

Using the reference properties at P_1 , V_1 , T_1 and S_1 , equation (21) will give $S_2 - S_{ref}$. Dropping the subscript 2 for generalizing the properties for any temperature and pressure, we have:

$$\underline{S} = (a-R)\ln T + bT + \frac{c}{2} T^2 + \frac{d}{3} T^3 + R\ln(\underline{V}-b) - \frac{B_2}{\underline{V}-b} - \frac{B_3}{2(\underline{V}-b)^2} - \frac{B_5}{4(\underline{V}-b)^4} + \left[\frac{C_2}{(\underline{V}-b)} + \frac{C_3}{2(\underline{V}-b)^2} + \frac{C_5}{4(\underline{V}-b)^4} \right] \frac{k}{T_c} e^{-\frac{kT}{T_c}} \quad (22)$$

$$+ Y$$

where $Y = S_{ref} - \left[(a-R)\ln T_{ref} + bT_{ref} + \frac{c}{2} T_{ref}^2 + \frac{d}{3} T_{ref}^3 + R\ln(\underline{V}_{ref}-b) - \frac{B_2}{\underline{V}_{ref}-b} - \frac{B_3}{2(\underline{V}_{ref}-b)^2} - \frac{B_5}{4(\underline{V}_{ref}-b)^4} + \frac{k}{T_c} e^{-\frac{kT_{ref}}{T_c}} \left(\frac{C_2}{\underline{V}_{ref}-b} + \frac{C_3}{2(\underline{V}_{ref}-b)^2} + \frac{C_5}{4(\underline{V}_{ref}-b)^4} \right) \right] \quad (23)$

Equation (22) is the final form for the entropy of the vapor and can be programmed for use on any digital computer. For a given set of constants of the heat capacity equation and the equation of state, the values of the vapor entropy can thus be run off.

- (vi) [b] The liquid entropy is the difference between the the vapor entropy and the entropy of vaporization. The procedure for obtaining these properties has been outlined above so that the liquid entropy can be obtained directly.

Superheated Vapor

The properties to be evaluated as functions of P and T or \underline{V} and T for the preparation of superheat tables are:

- (a). Volume or Pressure
- (b). Enthalpy
- (c). Entropy

In this case also, it is necessary to fix the range of temperature and the pressure or volume, whichever is desired. This is an arbitrary choice and depends mostly on the range which would be encountered in practice.

Having fixed these values, the following equations are to be solved for obtaining the various properties.

(a) The equation of state No. 3 is to be used. It will be solved by an explicit or implicit method depending on whether volume is fixed or is desired.

(b) For the known PVT conditions, the values of enthalpy and entropy are obtained from equations (15) and (22) respectively.

VI. MARTIN-HOU EQUATION OF STATE

WITH A₅ TERM

Martin and Hou examined the pressure-volume-temperature characteristics of pure gases in detail and developed an equation to fit the PVT characteristics of different gases. This equation requires only the critical properties and a low pressure point on the vapor pressure curve. The equation was used to check the PVT behavior of widely different gases and the agreement with the experimental data was excellent. It has later been used to correlate the PVT data for various "Freon" refrigerants with a high degree of accuracy.

The various hypothesis used in the development of this equation have been fully discussed in their paper entitled "Development of an Equation of State for Gases" (9). The conditions are summarized below:

1. $PV = RT$ as $P \rightarrow 0$
2. $(dP/dV)_T = 0$ at critical
3. $(d^2P/dV^2)_T = 0$ at critical
4. $(d^3P/dV^3)_T = 0$ at critical
5. $(d^4P/dV^4)_T = 0$ at critical
6. $\left[(dZ/dP_r)_{T_r} \right]_{P_r=0} = -(1-Z_c)$ at $T' = 0.8T_c$
7. $\left[(dZ/dP_r)_{T_r} \right]_{P_r=0} = 0$ at the Boyle point temperature
8. $(d^2P/dT^2)_V = 0$ at $V=V_c$
9. $(dP/dT)_V = M = -MP_c/T_c$ at $V=V_c$

The general form of the equation developed was:

$$P = \frac{RT}{(\underline{V}-b)} + \frac{A_2+B_2T+C_2e^{-\frac{kT}{T_c}}}{(\underline{V}-b)^2} + \frac{A_3+B_3+C_3e^{-\frac{kT}{T_c}}}{(\underline{V}-b)^3} + \frac{A_4}{(\underline{V}-b)^4} + \frac{B_5T}{(\underline{V}-b)^5} \quad (3a)$$

This equation was shown to predict the data up to densities of 1.3 times the critical within the experimental accuracy. Above these densities, it was found that the equation predicted too much curvature of the isometrics. This situation was improved by the addition of one more curvature constant, C_5 . The condition utilized to fix this constant was that at some very high density (approximately twice the critical density), the isometric is straight. Thus, the modified equation was:

$$P = \frac{RT}{(\underline{V}-b)} + \frac{A_2+B_2+C_2e^{-\frac{kT}{T_c}}}{(\underline{V}-b)^2} + \frac{A_3+B_3+C_3e^{-\frac{kT}{T_c}}}{(\underline{V}-b)^3} + \frac{A_4}{(\underline{V}-b)^4} + \frac{B_5T + C_5e^{-\frac{kT}{T_c}}}{(\underline{V}-b)^5} \quad (3b)$$

With the addition of this constant, the procedure for the evaluation of the constants was also modified. The changes in the various formulae were described in the "Freon-12", dichloro-difluoromethane, report (4).

The addition of the C_5 term did improve the curvature of the isometrics as was expected. However, the calculated values for "Freons-12, -23 and -C318" indicated that the equation predicted a higher slope of the isometrics at about 1.51 times the critical density. This led to further investigation of the characteristics of the isometrics at the higher densities.

From a study of the general trend of the isometrics at higher densities, it was concluded that the isometrics, in addition to being straight, have a definite slope which could be correlated with the slope of the critical isometric. This condition was finally taken as an additional hypothesis. It was thus possible to add one more constant to the equation. Since only the high density isometrics were subject for improvement, it was decided to add this constant preferably in the fifth or the fourth term. In the fifth term, with B_5 and C_5 already fixed, the only constant left was A_5 . Thus, two new equations with B_4 and A_5 terms

respectively were studied. It was found that the A_5 term did a better job in the correlation of the data, and so it was finally included in the equation. Thus, the final form of the modified Martin-Hou Equation is:

$$P = \frac{RT}{(\underline{V}-b)} + \frac{A_2+B_2T+C_2e^{-k\frac{T}{T_c}}}{(\underline{V}-b)^2} + \frac{A_3+B_3T+C_3e^{-k\frac{T}{T_c}}}{(\underline{V}-b)^3} + \frac{A_4}{(\underline{V}-b)^4} + \frac{A_5+B_5T+C_5e^{-k\frac{T}{T_c}}}{(\underline{V}-b)^5} \quad (3)$$

The addition of the A_5 term necessitated a revision of the procedure for the evaluation of constants. The various steps involved are given below.

PROCEDURE FOR EVALUATING THE CONSTANTS OF
THE MARTIN-HOU EQUATION OF STATE
WITH C_5 AND A_5 TERMS

The procedure for evaluating the constants of the equation with the B_5 term alone has been described in the paper by Martin and Hou (9). This procedure employed the nine conditions summarized earlier for the evaluation of the constants. The same formulae hold good for evaluating the temperature functions and the constants A_2 , B_2 , C_2 and A_4 even with the two additional conditions for the C_5 and A_5 terms. These formulae are reproduced below.

$$f_1(T_c) = RT_c \quad (24)$$

$$f_2(T_c) = 9P_c(\underline{V}-b)^2 - 3.8RT_c(\underline{V}_c-b) \quad (25)$$

$$f_3(T_c) = 5.4RT_c(\underline{V}_c-b)^2 - 17P_c(\underline{V}_c-b)^3 \quad (26)$$

$$f_4(T_c) = 12P_c(\underline{V}_c-b)^4 - 3.4RT_c(\underline{V}_c-b)^3 \quad (27)$$

$$f_5(T_c) = 0.8RT_c(\underline{V}_c-b)^4 - 3P_c(\underline{V}_c-b)^5 \quad (28)$$

$$b = \underline{V}_c \left(1 - \frac{B}{15Z_c} \right) \quad \text{where } Z_c = \frac{P_c \underline{V}_c}{RT_c} \quad (29)$$

$$C_2 = \frac{\left[f_2(T_c) + bRT' + \frac{(RT')^2}{P_c}(1-Z_c) \right] (T_B - T_c) + \left[f_2(T_c) + bRT_B \right] (T_c - T')}{(T_B - T_c) \left(e^{-k} - e^{-k T'/T_c} \right) - (T_c - T') \left(e^{-k T_B/T_c} - e^{-k} \right)} \quad (30)$$

$$B_2 = \frac{-f_2(T_c) - bRT_B - C_2 \left(e^{-k T_B/T_c} - e^{-k} \right)}{(T_B - T_c)} \quad (31)$$

$$A_2 = f_2(T_c) - B_2 T_c - C_2 e^{-k} \quad (32)$$

$$A_4 = f_4(T_c)$$

The derivation of expressions for the two remaining curvature term constants, C_3 and C_5 , has been given in the "Freon-12" report (4). The conditions utilized were:

1. $d^2P/dT^2 = 0$ at critical density
2. $d^2P/dT^2 = 0$ at n times critical density

Thus, we have:

$$\frac{d^2P}{dT^2} = \frac{C_2}{(\underline{V}-b)^2} + \frac{C_3}{(\underline{V}-b)^3} + \frac{C_5}{(\underline{V}-b)^5} = 0 \text{ at } \underline{V}_c \text{ and } \underline{V}_c/n \quad (33)$$

Therefore, eliminating C_5 and solving for C_3 in terms of C_2 , we have:

$$C_3 = \frac{C_2 \left[(\underline{V}_c - b)^3 - \frac{\underline{V}_c}{n} - b \right]^3}{\left[\left(\frac{\underline{V}_c}{n} - b \right)^2 - (\underline{V}_c - b)^2 \right]} \quad (34)$$

$$\text{and } C_5 = -C_2 (\underline{V}_c - b)^3 - C_3 (\underline{V}_c - b)^2 \quad (35)$$

The remaining constants to be evaluated are:

$$A_3, B_3, A_5, B_5$$

The conditions used for solving the constants are

- (i) At $\underline{V} = \underline{V}_c$, $\left(\frac{dP}{dT} \right)_{\underline{V}} = m$
- (ii) At $\underline{V} = \frac{\underline{V}_c}{n}$, $\left(\frac{dP}{dT} \right)_{\underline{V}} = N = y \text{ times } m$

$$\begin{aligned} \therefore \left(\frac{dP}{dT} \right)_{\underline{V}_c} &= \left(\frac{R}{\underline{V}_c - b} + \frac{B_2}{(\underline{V}_c - b)^2} + \frac{B_3}{(\underline{V}_c - b)^3} + \frac{B_5}{(\underline{V}_c - b)^5} \right) \\ &\quad - \left(\frac{C_2}{(\underline{V}_c - b)^2} + \frac{C_3}{(\underline{V}_c - b)^3} + \frac{C_5}{(\underline{V}_c - b)^5} \right) \frac{k}{T_c} e^{-k \frac{T}{T_c}} = m \end{aligned}$$

$$\text{and } \left(\frac{dP}{dT}\right)_{V=\frac{V_c}{n}} = \frac{R}{\frac{V_c}{n} - b} + \frac{B_2}{\frac{V_c}{n} - b} + \frac{B_3}{\frac{V_c}{n} - b} + \frac{B_5}{\frac{V_c}{n} - b} - \frac{k}{T_c} \frac{C_2}{\frac{V_c}{n} - b} + \frac{C_3}{\frac{V_c}{n} - b} + \frac{C_5}{\frac{V_c}{n} - b} \frac{k}{T_c} e^{-\frac{k}{T_c}}$$

$$= N = ym$$

where y is an arbitrary constant.

Eliminating B_5 from the above two equations, we have:

$$B_3 = \frac{m(V_c - b)^5 - N \left(\frac{V_c}{n} - b\right)^5}{(V_c - b)^2 - \left(\frac{V_c}{n} - b\right)^2} - R (V_c - b)^2 + \left(\frac{V_c}{n} - b\right)^2 - B_2 \frac{(V_c - b)^3 - \left(\frac{V_c}{n} - b\right)^3}{(V_c - b)^2 - \left(\frac{V_c}{n} - b\right)^2} \quad (36)$$

$$B_5 = m(V_c - b)^5 - R(V_c - b)^4 - B_2(V_c - b)^3 - B_3(V_c - b)^2 \quad (37)$$

$$A_3 = f_3(T_c) - B_3 T_c - C_3 e^{-k} \quad (38)$$

$$A_5 = f_5(T_c) - B_5 T_c - C_5 e^{-k}$$

The value of n is approximately 2.

VII. BIBLIOGRAPHY

1. Benning, A.F., and McHarness, R.C., Jackson Laboratory Report 30-89, No. 11, SN-15954.
2. Edgell, W.F., J. Amer. Chem. Soc., 69, 660(1947).
3. Physical and Thermodynamic Properties of "Freon 23", May, 1955, Engineering Research Institute, Ann Arbor.
4. Data and Equations for Some Thermodynamic Properties of "Freon-12", May, 1955, Engineering Research Institute, Ann Arbor.
5. Furukawa, G.T., McCosky, R.E. and Reilly, M.L., U.S. Bureau of Standards, Journal of Research 11-16, 52, January, 1954.
6. Graham, D.P., Jackson Laboratory Report, JLR-69-13, No. 13, SN-19333.
7. Lacher, Jackson Laboratory Report, JLR-71-3, No. 3, SN-19427.
8. Masi, J.F., Amer. Chem. Soc. J., 75, 5082-84, October 20, 1953.
9. Martin, J.J. and Hou, Y.C., J. Amer. Inst. Chem. Engr., Vol. 1, No. 2 (1955).
10. Naval Research Laboratory, NRL Report 3567.

