ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation and gratitude for the assistance of several people during the course of this work.

I wish to thank Professor Joseph J. Martin, chairman of my thesis committee, for his continuous and enlightening encouragement and guidance.

I would like to thank Professors Rane L. Curl, John E. Powers, Richard E. Sonntag and G. Brymer Williams for their constant help and advice.

I especially would like to thank Messrs. Soharab Hossain and Bipin P. Vora for their assistance in the laboratory work.

Many thanks are due to members of the Department of Chemical Engineering and the Department of Materials and Metallurgical Engineering staff including C. Bolen, D. Connell, P. Severn, F. Drogosz and J. Wurster who assisted in equipment problems. I would also like to thank Mr. Lloyd Swan for his assistance in computer programming.

I wish to thank Messrs. Andre Furtado and Bruce F. Caswell for several useful discussions during the course of this research.

I wish to thank Mr. J.C. Golba, Jr., and Miss Sue Bush for assistance in the preparation of this manuscript.

Many thanks are due to Mrs. Alvalea May for her typing and compilation of this dissertation.

In addition, I would also like to thank the following organizations for their equipment and financial support.

The E.I. du Pont de Nemours and Company generously supported the research project and supplied the substance under investigation, R-502.

The Industry Program of the College of Engineering of The University of Michigan supported the printing costs of this dissertation.

The Babcock and Wilcox Company and Mr. Rohinton K. Bhada allowed us to use their PVT equipment.

The Thermasan Corporation financially assisted by paying tuition.

Finally the author would like to thank his wife and family for their constant patience, encouragement and help.

TABLE OF CONTENTS

TABLE OF CONTENTS (contd.)

TABLE OF CONTENTS (contd.)

TABLE OF CONTENTS (contd.)

LIST OF TABLES

LIST OF TABLES (contd.)

LIST OF TABLES (contd.)

LIST OF TABLES (contd.)

LIST OF TABLES (contd.)

LIST OF TABLES (contd.)

LIST OF FIGURES

LIST OF FIGURES (contd.)

LIST OF FIGURES (contd.)

NOMENCLATURE

a_1,a_2,b_1,c_1,c_2	Constants used in the equation of state
A_1,B_1,C_1D_1	Constants used in the saturated liquid density equation
A,B,C,D,E	Constants in vapor pressure equation
$A_1,B_1,C_1,\ldots B_6$	Constants in the equation of state
$A_1',B_1',C_1',\ldots B_6'$	Constants in the equation of state
b_o	Volume factor in intermolecular potential energy
B	Second virial coefficient
C	Charge of a molecule
C	Third virial coefficient
d	Density and the distance parameter in the intermolecular potential energy function
e	Base of natural logarithm
f_2,f_3,f_4,f_5,f_6	Temperature functions in the equation of state
F	Symbol for functional relationship
G	Symbol for a property in general
J	Expression in mixing rule of Joffe
k	Boltzman constant
k	Exponential coefficient of temperature in the equation of state
K	Expression in mixing rule of Joffe
M	Vapor pressure parameter, Kihara potential parameter
N	Avagadro number
P	Pressure

NOMENCLATURE (contd.)

q	Quadrupole moment
r	Distance between molecules
R	Gas constant
S	Shape factor in Kihara potential
t	Temperature
T	Absolute temperature
U	Intermolecular potential energy
U_m	Minimum intermolecular potential energy
V	Kihara volume factor
V	Volume
$\underline{V}$	Specific volume
x	Mass fraction
y	Mole fraction
Z	Compressibility factor
α	Constant in mixing rule of Leland-Muell
α,β	Exponential coefficients in the intermo potential energy
Δ	Difference
ϕ	Azimuthal angle
μ	Dipole moment
ρ	Density
Σ	Summation
θ	Polar angle
ω	Accentric factor

NOMENCLATURE (contd.)

Subscripts

a,b	Substances a and b
b	To denote boiling point
b	To denote Boyle temperature
c	Critical point property
h	Height
i,j	Components in a mixture
m	Minimum property
mix	Mixture property
r	Reduced property
0	Reference property
1	Components 1
11	Component 1
12	Interaction between component 1 and component 2
2	Component 2
22	Component 2

Superscripts

c	Charge
μ	Dipole moment

Conversion Factors for Units Used in This Work

atm	14.696006 psi
bar	14.503830 psi
cu in	16.38670 ml
cu ft	28.317.017 ml
dyne/cm^2	1.4503830x10^{-5} psi
g	980.44 cm/sec^2, for Ann Arbor

NOMENCLATURE (contd.)

g_c	980.665 gm-cm/gmf-sec^2 (universal)
in	2.540051 cm
lb	453.59243 g
lb/cuft	0.016018369 g/cm^3
psi	51.7147 mmHg
R	10.73147 psi ft^3/(R)(lb mole)
R	F+459.67

ABSTRACT

PHYSICAL PROPERTIES AND INTERMOLECULAR POTENTIAL FUNCTIONS OF CHLORODIFLUOROMETHANE, CHLOROPENTAFLUOROETHANE AND THEIR MIXTURE OF COMPOSITION: CHLORODIFLUOROMETHANE, 48.8WT.% AND CHLOROPENTAFLUOROETHANE 51.2WT.%

by

Vasant Lotu Bhirud

Chairman: Joseph J. Martin

Objectives of this research were: (1) to determine experimentally PVT behavior, vapor pressure and critical temperature of the azeotropic mixture (R-502) containing chlorodifluoromethane (R-22), 48.8Wt.% and chloropentafluoroethane (R-115), 51.2Wt.%, (2) to correlate the mixture experimental data algebraically, (3) to correlate literature values of properties of the components and formulate methods of prediction of properties of the mixture and (4) to analyze the second virial data for the components and the mixture to obtain characteristic intermolecular potential energy parameters by a new analytical method.

PVT behavior of the mixture R-502 was determined over a temperature range of 100 to 250 F, pressure range of 80 to 2000 psia and densities up to two times the critical density. Experimental determinations were made using a bellows PVT cell capable of volume expansion of 14:1. Vapor pressure measurements covered a temperature range of 100F to the critical temperature.

The PVT data of R-502 as well as its pure components R-22 and R-115 were fitted by an equation of the form,

$$P = \frac{RT}{V-b} + \frac{A_2+B_2T+C_2e^{-kT}}{(V-b)^2} + \frac{A_3+B_3T+C_3e^{-kT}}{(V-b)^3} + \frac{A_4+B_4T+C_4e^{-kT}}{(V-b)^4} + \frac{A_5+B_5T}{e^{a_1v}(1+C_1e^{a_1v})} + \frac{A_6+B_6T}{e^{a_2v}(1+C_2e^{a_2v})}$$

The vapor pressure data was correlated by the following equation:

$$\ell nP = A + \frac{B}{T} + C\ell nT + DT + \frac{E(F-T)}{FT}\ \ell n(F-T)$$

Saturated liquid densities obtained in earlier work were correlated by the following equation.

$$d_s = A + B(1-T_R)^{1/3} + C(1-T_R)^{2/3} + D(1-T_R) + E(1-T_R)^{4/3}$$

In order to predict the properties of the azeotrope R-502 from the properties of its components, it was found necessary to predict the critical values of R-502 precisely. The critical volume and temperature were predicted by the following equations:

$$V_{cm} = x_1 V_{c1} + x_2 V_{c2}$$

$$\frac{T_{Bm}}{T_{cm}} = x_1 \frac{T_{B1}}{T_{c1}} + x_2 \frac{T_{B2}}{T_{c2}}$$

A new method was used to predict the critical pressure of the mixture and is given by the following equation:

$$\frac{1}{P_{cm}} = \frac{x_1}{P_{c1}} + \frac{x_2}{P_{c2}}$$

A simplified method was used to determine two characteristic parameters of a modified Lennard-Jones intermolecular potential function from the second virial data. The second virial coefficient is given by the resulting equation,

$$B(T) = 8\pi N\, d_o^3 \left[\frac{1}{15} + \frac{2}{9}\frac{U_m}{kT} - \frac{16}{315}\left(\frac{U_m}{kT}\right)^2\right]$$

The second virial coefficients for the mixture were predicted from the intermolecular potential energy parameters of the pure components.

It is expected that other refrigerant mixtures could be treated by the methods developed here.

THE UNIVERSITY OF MICHIGAN

INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

PHYSICAL PROPERTIES AND INTERMOLECULAR POTENTIAL FUNCTIONS OF CHLORODIFLUOROMETHANE, CHLOROPENTAFLUOROETHANE AND THEIR MIXTURE OF COMPOSITION: CHLORODIFLUOROMETHANE, 48.8WT.% AND CHLOROPENTAFLUOROETHANE 51.2WT.%

Vasant Lotu Bhirud

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy in the
University of Michigan
Department of Chemical Engineering
1973

April, 1973

IP-851

[illegible]

[illegible] days

CHAPTER I

INTRODUCTION

Midgley and Henne (102) first suggested that chlorofluoro derivatives of organic compounds could be used for refrigeration. Since then many compounds have been developed for commercial use. Azeotropic mixtures of refrigerants are unique in behavior in that their liquid and vapor phases have the same composition over a considerable range of temperatures and therefore practically no fractionation can occur in the refrigeration equipment in the event of a leak. One of such azeotropic mixtures is the mixture termed as R-502* which contains 48.8 wt% (63 mol %) chlorodifluoromethane (R-22*) and 51-2 wt % (37 mol %) chloropentafluoroethane (R-115*). Benning (11) patented this azeotrope in 1953 and it was introduced to the commercial market in 1962 by the Du Pont Company. This azeotrope has a normal boiling point of about -46 C. Refrigeration performance characteristics of R-502 have been published in the literature (33, 43, 45, 96, 111, 112, 130). Azeotrope R-502 has been found superior to an other popular refrigerant R-22 (43).

In the design of refrigerating equipment, it is essential to know the physical and thermodynamic properties of refrigerant under consideration. Preliminary tables of thermodynamic properties of R-502 were published by Du Pont Company in 1963 (47) which were based on a few experimental determinations of vapor pressure and generalized correlations applicable to mixtures. Badylkes (5,6,7) developed similar tables

---

*Name assigned by ASHRAE.

of thermodynamic properties in metric units for R-502 based on Du Pont's vapor pressure data and corresponding states theory. In 1967, Loffler (86) published results of experimental determinations of vapor pressure, saturated liquid density and critical temperature of R-502, but did not give any experimental data.

Considering the limited amount of experimental data, this work was initiated in 1966. Objectives of this project are to determine experimentally following physical properties of R-502.

1. Pressure-volume-temperature (henceforth will be abbreviated to "PVT" behavior of the gas.
2. Vapor pressure of saturated liquid
3. Saturated liquid densities
4. Critical constants

Further intent of the thesis was to use a variable volume technique to make PVT determinations. There are very few PVT cells with this capability and they are reviewed later. The PVT cell used in this study was first designed and used by Bhada (15). This cell consists of stainless steel bellows capable of giving a volume expansion of at least tenfold. During the experimentation the gas under study does not come into contact with any liquids and therefore the cell may be termed as a dry cell. The versatility of this PVT cell is enormous. In this investigation we improved the techniques of data measurements. First we used mercury as the hydraulic fluid which is used to compress the bellows. Levels of hydraulic fluid in a glass tube reservoir were measured by a cathetometer. Temperature control of the bath was improved by putting extra insulation and using carefully placed auxiliary knife heaters.

For the other properties, well known experimental equipment and apparatus described by Hou (62) are used.

A further object of this thesis is to correlate these properties algebraically. To describe the vapor pressure of R-502, Martin, Kapoor and Shinn's equation (93) is used. Saturated liquid density data is correlated by the Martin-Hou equation (91).

Algebraic correlations of PVT data using Martin's equation (89) were studied in detail and it is found necessary to modify the original techniques so as to be able to cover a wider range of experimental data.

It was further the purpose of this work to formulate the methods of predicting algebraically the properties of R-502 from the properties of its components. The outcome of this study is the formulation of methods of predicting critical constants for azeotropes such as R-502.

It was the object of this thesis to initiate intermolecular potential energy studies for chlorofluoro derivatives of organic compounds. An extensive literature study is presented on this subject. Several models are available for the potential energy of interaction between two molecules out of which the Lennard-Jones model (85) is selected. A new algebraic method of evaluating the parameters of Lennard-Jones' model is presented here.

Thus the total work covers experimental measurements of physical properties of R-502 and their algebraic correlations, algebraic correlations of physical properties of the components R-22 and R-115, methods of predicting algebraically the mixture properties and finally the intermolecular potential energy studies of components as well as the mixture R-502.

II. LITERATURE REVIEW

The literature survey is divided into three major sections as follows:

A) Physical properties of R-22, R-115 and R-502

B) Variable volume equipment for PVT measurements

C) Intermolecular potentials

As noted in Chapter I, physical properties selected for this review are:

1) PVT behavior of gas
2) Vapor pressure of saturated liquid
3) Density of saturated liquid
4) Critical pressure, volume and temperature.

For PVT measurements various equipment are used, section B deals with only variable volume equipment. In section C several analytical equations available to describe intermolecular potential energy are reviewed.

A. PHYSICAL PROPERTIES OF R-22, R-115 AND R-502

A-1. Physical properties of R-22

Table II-1 lists works on the physical properties of R-22. Each work is discussed below.

A-1. (a) PVT Behavior of R-22

Ranges of experimental determinations of PVT behavior of R-22 are given in Table II-2 and Figure II-1.

Benning and McHarness (13) investigated PVT behavior of R-22. They used material obtained by multiple distillations of commercial grade R-22. Purity of the material was checked by determining freezing point and limiting vapor density measurements. Low pressure (0.3 to 2 atm.) vapor density measurements gave an apparent molecular weight of

TABLE II-1

PHYSICAL PROPERTIES OF R-22

PVT Behavior	Vapor Pressure	Saturated Liquid Density	Critical Constants
1) Benning and McHarness (1940)...(13)	1) Booth and Swinehart (1935)...(17)	1) Benning and McHarness (1940) ...(14)	1) Booth and Swinehart (1935)...(17)
2) Michels (1957)...(99)	2) Benning and McHarness (1940)...(12)	2) DuPont Bulletin T-22 (1964)..(46)	2) Benning and McHarness ...(14)
3) Du Pont Bulletin T-22 (1964)...(46)	3) Klezkii (1964)...(80)	3) Zander (1968)...(140)	3) Du Pont Bulletin T-22 (1964)...(46)
4) Lagutina (1966)...(83)	4) Du Pont Bulletin T-22 (1964)...(46)		4) Martin (1967)..(89)
5) Zander (1968)..(140)	5) Lagutina (1966)..(83)		5) Zander (1968)..(140)
	6) Zander (1968)..(140)		

TABLE II-2

RANGES OF PVT MEASUREMENTS FOR R-22

Property	Units	Maximum Value	Minimum Value	Critical Value	Maximum Reduced Value	Minimum Reduced Value	Reference
P	psia	310	4	715.7	0.433	0.006	Benning and McHarness (13)
T	R	743.67	536.67	664.47	1.12	0.808	
ρ	lbs/cu.ft.	4.961	0.057	34.46	0.144	0.0016	
P	psia	1880	93	721.9	2.61	0.1288	Michels (99)
T	R	762	525	664.50	1.15	0.790	
ρ	lbs/cu.ft.	41.97	1.610	32.76	1.280	0.049	
P	psia	3030	225	723.74	4.19	0.313	Zander Isometric Data (140)
T	R	745.2	516.6	664.79	1.12	0.777	
ρ	lbs/cu.ft.	77.97	5.15	32.03	2.435	0.161	
P	psia	5080	145	723.74	7.02	0.20	Zander Isothermal Data (140)
T	R	851.4	545.4	664.79	1.28	0.821	
ρ	lbs/cu.ft.	-	-	32.03	-	-	

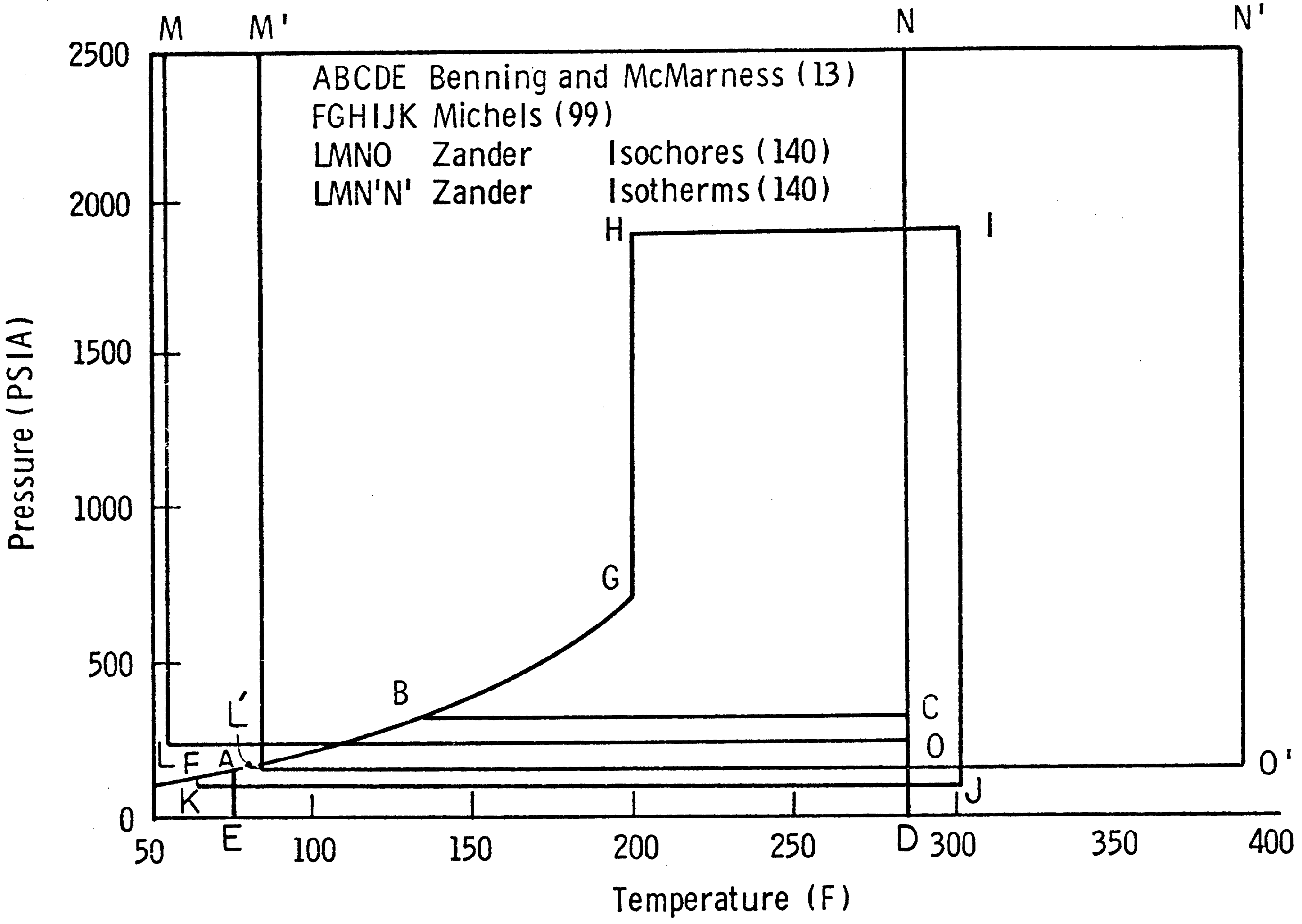

Fig. II. 1. Ranges of PVT Measurements for R-22

R-22 as 87.25 instead of the theoretical value of 86.46. This was attributed initially to impurity in R-22 and further purification by distillation at pressures of one and 0.2 atm. was carried out. Different fractions of the distillation had the same apparent molecular weight. Results of chemical analysis for chlorine and fluorine were inconclusive to solve this discrepancy. No other explanation was found for the anomalous molecular weight of R-22. In correlating PVT data, low pressure vapor density measurements were brought into agreement with the rest of the data by using a multiplier, k, to gas constant R in the Beattie-Bridgeman (9) equation of state. Mass recovery for PVT measurements was precise to 0.3% max. at lowest density and 0.06% max. at the highest density. Temperature of a bath surrounding the PVT cell was controlled to ±0.1 C. Pressure was measured by Bourdon gauges. Constant volume cell was used for PVT measurements. Correlation of forty data points resulted in the following equation:

$$P = 0.08132T\,D + (0.015044\,T-12.69)\,D^2 + (0.013796\,T-3.794)D^3 \ldots \qquad \text{(II-1)}$$

where P = pressure, atm. abs.

T = temperature, K

D = molar density, moles per liter

R = 0.08206 (liter) (atm)/(g-mole)(K)

Eqn. II-1 predicted experimental pressures with average deviation of 0.3%.

Michels (99) used variable volume equipment to obtain isothermal PVT data. His 181 data points were correlated to Martin-Hou equation by Martin (89). The equation of state for R-22 is:

$$P = \frac{RT}{(v-b)} + \sum_{i=2}^{5} \frac{Ai + Bi + Ci\ e^{-kT}}{(v-b)i} + \frac{A_6 + B_6\ T + C_6\ e^{-kT}}{e^{av}} + \frac{A_7 + B_7\ T + C_7\ e^{-kT}}{e^{2av}} \qquad \text{(II-2)}$$

where $R = 0.124098$

$A_2 = -4.353547$

$B_2 = 2.407252 \times 10^{-3}$

$C_2 = -44.066868$

$A_3 = -0.017464$

$B_3 = 7.62789 \times 10^{-5}$

$C_3 = 1.483763$

$A_4 = 2.310142 \times 10^{-3}$

$B_4 = -3.605723 \times 10^{-6}$

$C_4 = 0$

$A_5 = -3.724044 \times 10^{-5}$

$B_5 = 5.355465 \times 10^{-8}$

$C_5 = -1.845051 \times 10^{-4}$

$A_6 = 1.363387 \times 10^{8}$

$B_6 = -1.672612 \times 10^{5}$

$C_6 = A_7 = B_7 = C_7 = 0$

$a = 548.2$

$b = 0.002$

$k = 4.2/Tc$

$Tc = 664.50°R$

$Pc = 721.906$ psia

$Vc = 0.030525$ ft^3/lb

°R = °F + 459.69

Eqn. II-2 predicted experimental values of pressure with an average deviation of -0.01%, average absolute deviation of 0.07% and maximum deviation of 0.61%.

An equation of state for R-22 was published by Du Pont Company (46). This equation was based on Michels (99) data and unpublished data at The University of Michigan. Eqn. II-2 supercedes the equation of state for R-22 given by the Du Pont Company (46).

Lagutina (83) obtained 74 PVT data points which are not available. This data was compared by Zander (140) with his own data.

Zander (140) studied PVT behavior of R-22 taking 163 isometric and 107 isothermal data points. Purity of R-22 was 99.97%. His estimated precision of experimental measurements for isometric data points were: pressure: ±0.01%, temperature: ±0.01% and volume: ±0.1%. Isothermal data points were obtained by using Burnett's apparatus (27). Maximum estimated error in the compressibility factors for isothermal data was 0.25%. All data was correlated by equation of state described by Stein (131) and is given as:

$$K(\tau,\ \varepsilon) = \sum_{i=0}^{7} \left(\sum_{j=0}^{2} C_{i,j}\ \tau^{j} \right) \varepsilon^{i} \qquad \text{(II-3)}$$

where

$$\tau = 1 - \frac{1}{\theta},\ \varepsilon = \frac{1}{\phi} - 1$$

$$\theta = \frac{T}{Tc},\ \phi = \frac{V}{Vc},\ \sigma = \frac{R\ Tc}{PcVc},\ \pi = \frac{P}{Pc} \qquad \text{(II-4)}$$

$$\left(\frac{\pi\phi}{\sigma\theta} - 1\right)\phi = [Z(\theta - \phi) - 1]\phi = K(\theta,\phi)$$

Coefficients in the eqn. II-3 are given in Table II-3.

TABLE II-3

COEFFICIENTS IN THE EQUATION II-3 FOR R-22(131)

	j = o	j = 1	j= 2
C_{0}, j	-0.726090	1.597642	0.546733
C_{1}, j	0.452179	-1.079114	2.293855
C_{2}, j	-0.178269	1.656474	-3.320042
C_{3}, j	0.008353	0.617720	-1.094151
C_{4}, j	0.184597	-1.005899	1.828942
C_{5}, j	0.034258	-0.170070	-0.369520
C_{6}, j	-0.043901	0.190471	0
C_{7}, j	-0.001196	0	0

Zander (140) used eqn. II-4 with values of coefficients given in Table II-3 to compare his and other available data (13, 83) and the results are summarized in terms of average percent deviation in Table II-4.

TABLE II-4

MEAN DEVIATIONS OF PREDICTED VALUES BY EQN. II-3 FROM EXPERIMENTAL DATA (140)

Experimental Work	Average Percent Deviation in V	Average Percent Deviation in P
1. Zander's (140) isothermal data	±0.18%	±0.34%
2. Zander's (140) isometric data	±0.69%	±0.48%
3. Forty data points of Benning and McHarness (13)	±1.07%	±1.18%
4. Seventy-four data points of Lagutina (83)	±0.50%	±0.85%

This completes the literature review of the PVT behavior of R-22.

A.1 (b) Vapor Pressure of R-22

Ranges of experimental vapor pressure determinations for R-22 are given in Table II-5.

Booth and Swinehart (17) measured vapor pressure of R-22 using a cailletet tube. Temperature control was of the order of ±0.01 C. Pressure readings were accurate to within 0.1 atm. Nineteen data points are available which were not fitted to any analytical equation.

Benning and McHarness (12) measured vapor pressure at six temperatures. They used same material as was used for PVT determinations (section II-A.1(a)). Temperature control was accurate to ±0.01 C and

TABLE II-5

RANGES OF VAPOR PRESSURE MEASUREMENTS FOR R-22

Property	Units	Minimum Value	Maximum Value	Critical Value*	Minimum Reduced Value	Maximum Reduced Value	Reference
P	psia	138	707.90	712.46	0.194	0.994	Booth and Swinehart (17)
T	R	532.35	665.01	664.48	0.80	1.00	
P	psia	5	674.84	715.7	0.007	0.943	Benning and McHarness (12)
T	R	381.40	658.35	664.47	0.547	0.989	
P	psia	0.08	692	721.9	0.0001	0.959	Du Pont Bulletin T-22 (46)
T	R	304.67	664.48	664.48	0.459	1.00	
P	psia	3	709.19	723.74	0.004	0.980	Zander (140)
T	R	365.98	622.85	664.79	0.55	0.995	

*Critical constants of Du Pont Bulletin T-22 (46) are assumed when not available in the reference.

pressure measurements were precise to 0.3% or better. Vapor pressure data was fitted to the following equation.

$$\log_{10} P = A + \frac{B}{T} + C \log_{10} T + D\,T \qquad \text{(II-5)}$$

where

P = pressure in absolute atmospheres

T = Degrees Kelvin = °C + 273.10

$A = 25.1144$ $\quad$ $C = -8.1418$

$B = -1638.82$ $\quad$ $D = 0.0051838$

Eqn. II-5 predicts their own data with an average absolute deviation of 0.4%, with maximum deviation of -0.6%. Data points of Booth and Swinehart (17) were predicted by Eqn. II-5 to average absolute deviation of 1.66% with maximum deviation of +3.58%.

Klezkii (80) used static method for vapor pressure measurements, composition of R-22 used by him was 99.85 mole %, R-22, 0.1 mole %, R-12 and R-13, 0.05 mole %, CO_2. Experimental equipment was checked for precision by measuring vapor pressure of water and carbon dioxide. He correlated his data by the following equation.

$$P = 13.51222 - \frac{1404.99}{T} - 3.15464 \log T + 3.4953 \times 10^{-17}\, T^6 \qquad \text{(II-6)}$$

where P = pressure in 10^{-5} Newtons/m^2

T = temperature in degrees Kelvin

Eqn. II-6 predicts his data with a maximum deviation of 0.06% (80). Experimental vapor pressure data points of Klezkii (80) are not available.

Du Pont Company (46) published a vapor pressure equation of R-22 based on Michel's data (99) and unpublished data from The University of Michigan. The equation is:

$$\log_{10} P = A - \frac{B}{T} - C \log_{10} T + D\,T + \frac{E(F-T)}{F\ T} \log_{10}(F-T) \qquad \text{(II-7)}$$

where P = pressure in psia

T = temperature in degrees Rankine = °F + 459.69

$A = 29.35754453$ $D = 0.002190939044$

$B = 3845.193152$ $E = 305.8268131$

$C = 7.86103122$ $F = 686.1$

Eqn. II-7 predicted Michel's data (99) and unpublished data from The University of Michigan with an average deviation of 0.11% (46).

Lagutina (83) took twenty vapor pressure data points for R-22 which are not available but were compared with his own data by Zander (140).

Zander (140), using static method, obtained twenty three vapor pressure data points. Temperature measurements were accurate to ±0.01 C and pressure values to ±0.01%. He correlated his data using the following equation:

$$\theta \log \pi = \sum_{i=0}^{5} A_i (1 - \theta)^i \qquad \text{(II-8)}$$

where $\theta = T/T_c$ $\pi = P/P_c$

$A_o = 0$ $A_3 = -4.325804$

$A_1 = -2.967411$ $A_4 = 6.571489$

$A_2 = 1.264675$ $A_5 = -5.903528$

Predicted values by Eqn. II-8 were compared by Zander (140) with his and other's (12,80,83) data and results are summarized in Table II-6.

TABLE II-6

MEAN DEVIATIONS OF CALCULATED VALUES BY EQN. II-8
FROM EXPERIMENTAL DATA (II-8)

Reference	No. of Data Points	Average Percent Deviation
1. Booth and Swinehart (17)	18	± 1.95
2. Benning and McHarness (12)	7	± 0.35
3. Klezkii (80)	14	± 0.09
4. Lagutina (83)	20	± 0.54
5. Zander (140)	23	± 0.07

A.1 (c) Saturated Liquid Density of R-22

Ranges of experimental saturated liquid density measurements are given in Table II-7.

Benning and McHarness (14), using sealed tube method and obtained nine saturated liquid density points for R-22. Material was same as used for PVT measurements (section II-A.1(a)). Temperature measurements were precise to 0.1 C. They correlated their experimental data by the following equations:

For temperatures between -70 and 25°C

$$d_s = 1.2849 - 0.003450\ t - 0.0000073\ t^2 \qquad \text{(II-9)}$$

TABLE II-7

RANGES OF SATURATED LIQUID DENSITY MEASUREMENTS FOR R-22

Property	Units	Minimum Value	Maximum Value	Critical Value*	Minimum Reduced Value	Maximum Reduced Value	Reference
ds	lbs/cu.ft.	51.0	93.1	34.46	1.48	2.70	Benning and McHarness (14)
T**	R	658.83	367.47	664.47	0.99	0.553	
ds	lbs/cu.ft.	51.0	100.0	32.76	1.56	3.05	Du Pont Bulletin T-22 (46)
T**	R	650.0	304.67	664.48	0.979	0.459	
ds	lbs/cu.ft.	47.2	80.0	32.03	1.47	2.50	Zander (140)
T**	R	656.28	486.67	664.79	0.988	0.733	

*Critical constants of Du Pont Bulletin T-22 (46) are assumed when not available in the reference.
**Temperature values correspond to the density figures.

For temperatures between 25 and 65°C

$$d_s = 1.2652 - 0.002109\ t - 0.000298\ t^2 \qquad \text{(II-10)}$$

where d_s = density in g/cc

t = Temperature in degrees centigrade

Eqns. II-9 and II-10 predict their data with a maximum deviation of 0.01%.

Du Pont Company (46) published a saturated liquid density equation based on unpublished data of their own and from University of Michigan. The equation is:

$$d_s = A+B\left(1-\frac{T}{Tc}\right)^{1/3} + C\left(1-\frac{T}{Tc}\right)^{2/3} + D\left(1-\frac{T}{Tc}\right) + E\left(1-\frac{T}{Tc}\right)^{4/3} \qquad \text{(II-11)}$$

where d_s = Saturated liquid density in lbs/cu.ft.

T = temperature in degrees Rankine = °F + 459.69

T = 664.5 R

A = 32.76

B = 54.6344093

C = 36.74892

D = -22.2925657

E = 20.47328862

Eqn. II-11 predicted experimental points with an average deviation of 0.08%.

Zander (140), using calibrated glass pycnometer measured saturated liquid density of R-22 at thirty one temperatures. Estimated precision of density values was ± .0.1% except near the critical point. He correlated his experimental data by the following equation:

$$d_R = \sum_{j=0}^{4} D_j \, (1-\theta)^{j/2} \qquad \text{(II-12)}$$

where d_R = density of saturated liquid/critical density

$\theta = T/T_c$

T_c = 664.79 R $\qquad D_2 = -9.687052$

$D_o = 1.0$ $\qquad D_3 = 16.888054$

$D_1 = 4.936493$ $\qquad D_4 = -10.978106$

Eqn. II-12 predicts data of Benning and McHarness (14) with deviations up to 2.8% and that of Zander (140) with average absolute deviation of 0.01% and maximum deviation of 0.011%.

A.1 (d) Critical Constants of R-22

Table II-8 lists critical constants of R-22 as determined by different workers.

A-2. Physical Properties of R-115

Table II-9 lists authors of papers dealing with physical properties of R-115 under each property. These works are discussed below.

A.2(a) PVT Behavior of R-115

Ranges of experimental PVT measurements are given in Table II-10 and Fig. II-2.

Sixty one unpublished experimental PVT data points determined at The University of Michigan (136) were available. PVT data was taken using constant volume method. Sample of R-115 had an air composition of 0.0045% of the vapor. Mass recovery was within 0.28%, and usually less than 0.04% of mass charged. Experimental data was correlated by the following equation.

TABLE II-8

CRITICAL CONSTANTS OF R-22

Critical Temp. R	Critical Pressure psia	Critical Volume ft^3/lb	Critical Density lb/ft^3	Critical Compressibility Factor	Reference
665.19	712.46	-	-	-	Booth & Swinehart (17)
664.47	715.7	0.029019	34.46	0.25182	Benning and McHarness (14)
664.48	721.906	0.030525	32.76	0.2673	Du Pont Bulletin T-22 (46)
664.48	721.906	0.030525	32.76	0.2673	Martin (89)
664.79	723.74	0.031221	32.03	0.27394	Zander (140)

TABLE II-9

PHYSICAL PROPERTIES OF R-115

PVT Behavior	Vapor Pressure	Saturated Liquid Density	Critical Constants
1) University of Michigan (1951)...(136)	1) University of Michigan (1951)...(136)	1) Downing (1949)...(41)	1) University of Michigan (1951)...(136)
2) Loeffler and Matthias (1966)...(87)	2) Aston, Wills, and Zolki (1955)...(4)	2) University of Michigan (1951)...(136)	2) Loeffler and Matthias (1966)..(87)
3) Mears et al. (1966) ...(98)	3) Loeffler and Matthias (1966)...(87)	3) Loeffler and Matthias (1966)...(87)	3) Mears et al. (1966) ...(98)
	4) Mears et al. (1966) ...(98)	4) Mears et al. (1966) ...(98)	

TABLE II-10

RANGES OF PVT MEASUREMENTS FOR R-115

Property	Units	Maximum Value	Minimum Value	Critical Value	Maximum Reduced Value	Minimum Reduced Value	Reference
P	psia	1015	175	457.93	2.22	0.385	Mears et al. (98)
T	R	806.4	563.4	635.58	1.27	0.887	
ρ	lbs/cu.ft.	55.23	6.18	38.27	1.443	0.162	
P	psia	1300	34	453.0	2.84	0.0744	University of Michigan (136)
T	R	887	470	635.56	1.395	0.737	
ρ	lbs/cu.ft.	42.01	1.1350	37.2	1.101	0.0305	

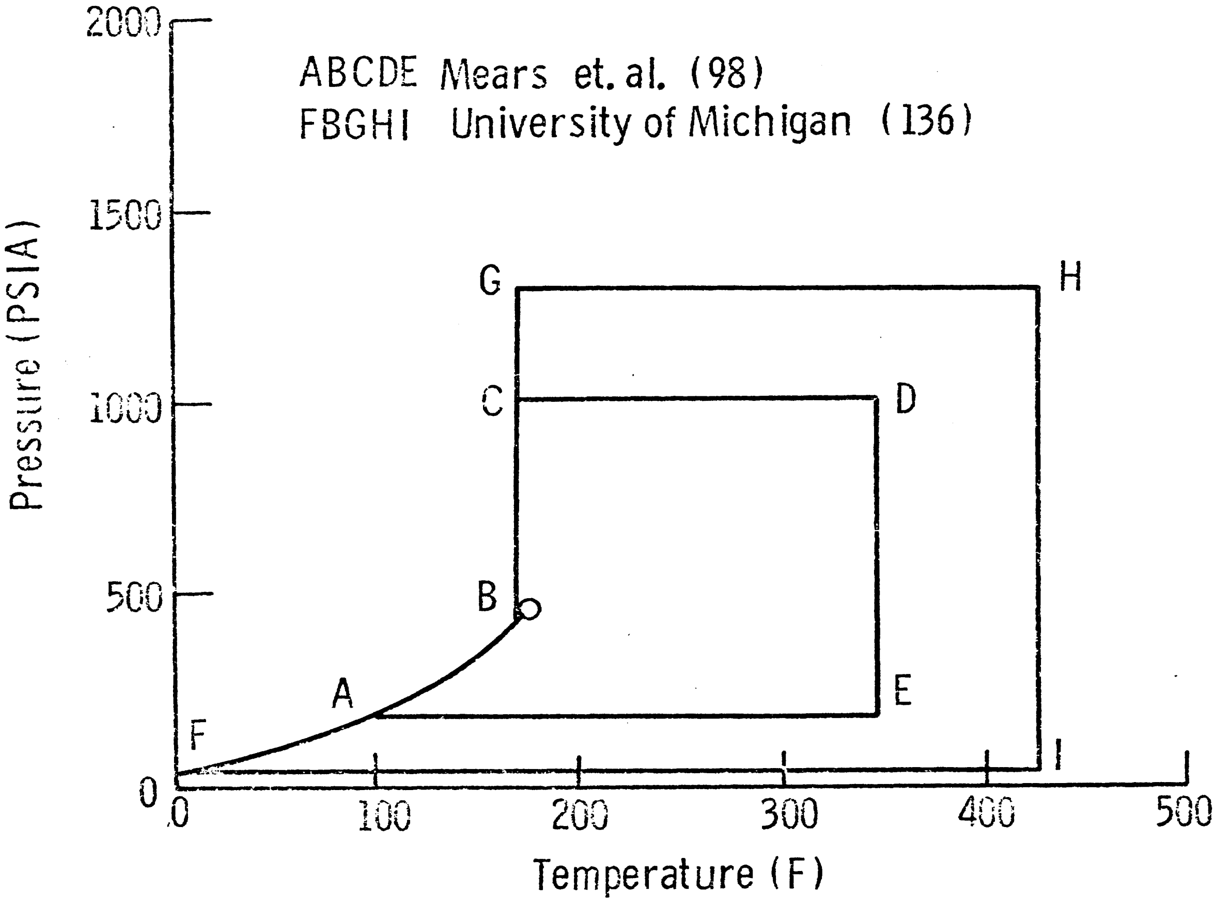

Fig. II. 2 Ranges of PVT Measurements for R-115

$$P = A + B\,T - \frac{C}{T^3} \qquad \text{(II-13)}$$

where

$$A = \frac{-3.1857748}{v^2} + \frac{0.028919059}{v^3} - \frac{17.4448 \times 10^{-6}}{v^4}$$

$$B = \frac{0.06941}{v} + \frac{0.00267975}{v^2} - \frac{1.18424 \times 10^{-5}}{v^3} - \frac{1.67627 \times 10^{-7}}{v^4}$$

$$C = \frac{8.343505 \times 10^6}{v^2} - \frac{5984.903}{v^4}$$

P = pressure in psia

V = volume in ft^3/lb

T = temperature, °R = °F + 459.69

Eqn. II-13 predicted sixty-one experimental data points with an average deviation of 0.56% up to the critical density.

Loffler and Matthias (87) obtained experimental PVT data for R-115 which is not available, but the correlating equation is:

$$P = \sum_{i=1}^{5} \frac{A_i + B_i\,T + C_i \exp\left(-k\,T/T_c\right)}{(v - b)^i} \qquad \text{(II-14)}$$

where

P = pressure in kg/m^2

T_c = 353.15 K (K = C + 273.15)

v = volume in m^3/kg

$A_1 = C_1 = B_4 = C_4 = 0$

$k = 5.475$

$b = 0.375621948 \times 10^{-3}$

$B_1 = 0.548844475 \times 10^{-3}$ (gas constant)

$A_2 = -0.630246499 \times 10^{-3}$

$B_2 = 0.571969964 \times 10^{-6}$

$C_2 = -0.105686282 \times 10^{-1}$

$A_3 = 0.611915189 \times 10^{-6}$

$B_3 = -0.285392832 \times 10^{-9}$

$C_3 = 0.159305901 \times 10^{-4}$

$A_4 = -0.354925144 \times 10^{-9}$

$A_5 = 0.823490309 \times 10^{-13}$

$B_5 = 0.568119622 \times 10^{-16}$

$C_5 = -0.351035219 \times 10^{-11}$

Mears et al. (98), using a constant volume method obtained 90 experimental PVT data points. Samples of R-115 had a purity of better than 99.9 mole %. Estimated precision in pressure measurements was ±0.02% or better, in temperature measurements ±0.05% and in volume measurements, ±0.1% or better. Mass recovery was within ±0.03%. Experimental PVT data was correlated by BWR (10) and Martin-Hou (91) equations of state and the equations are given in Table II-11.

TABLE II-11

EQUATIONS OF STATE FOR R-115

1) Benedict-Webb-Rubin Equation (10)

$$P = \frac{RT}{V} + \frac{B_o R T - A_o - C_o/T^2}{V^2} + \frac{b R T - a}{V^3} + \frac{a \alpha}{V^6} + \frac{C}{T^2} \left(\frac{1}{V^3} + \frac{\gamma}{V^5} \right) e^{-\gamma/V^2} \qquad \text{(II-15)}$$

where P = pressure in atmospheres

V = volume in cc/g

T = temperature in degrees Kelvin

R = 0.531179 (ml) (atm.)/(K)(g)

$A_o = 8.16931 \times 10^1$

$B_o = 0.1124173$

$C_o = 4.062018 \times 10^7$

$\alpha = 0.20052475$

$\gamma = 1.22$

$a = 9.216943 \times 10^2$

$b = 3.0806914$

$c = 7.675972 \times 10^7$

2) Martin-Hou Equation (91)

$$P = \frac{RT}{V-b} + \sum_{i=2}^{5} \frac{A_i + B_i T + C_i e^{-kT/T_c}}{(V-b)^i} \tag{11-16}$$

where

P = pressure in atmospheres

V = volume in cc/g

T = temperature in degrees Kelvin

R = 0.531179 (ml)(atm.)/(K)(g)

$T_c = 353.1$ K

$b = 0.3813516$

$K = 5.475$

$B_3 = -0.5123829$

$C_3 = 1.179472 \times 10^4$

$A_4 = -3.299045 \times 10^2$

$A_2 = -6.720228 \times 10^{2}$

$B_2 = 7.204497 \times 10^{-1}$

$C_2 = -8.12817 \times 10^{3}$

$A_3 = 6.764326 \times 10^{2}$

$B_4 = C_4 = 0$

$A_5 = 1.379499 \times 10^{1}$

$B_5 = 0.2091698$

$C_5 = -1.742745 \times 10^{3}$

Experimental PVT data for R-115 was predicted by BWR equation of state within an average deviation of 0.26% and maximum deviation of 1.1%. Respective figures for Martin-Hou equation were 0.34% and 1.2%. Values predicted by Eqn. II-1_3 on comparison with BWR equation of state showed average deviation of 1% except at high density isochor where deviation amounting to 15% was encountered.

A.2(b) Vapor Pressure of R-115

Ranges of experimental vapor pressure measurement are given in Table II-12.

Twelve vapor pressure data points for R-115 were obtained by static method at The University of Michigan (136). A sample of R-115 had an air composition of 0.0032% of vapor. Experimental data was correlated by the following equation:

$$\log P = -\frac{66911.9}{T^2} - \frac{1879.080}{T} + 7.118882 - 0.00375058\ T + 2.58213 \times 10^{-6}\ T^2 \qquad \text{(II-17)}$$

TABLE II-12

RANGES OF VAPOR PRESSURE MEASUREMENTS FOR R-115

Property	Units	Minimum Value	Maximum Value	Critical Value*	Minimum Reduced Value	Maximum Reduced Value	Reference
P	psia	0.55	453	453.0	0.0012	1.00	University of Michigan (136)
T	R	324.13	635.56	635.56	0.51	1.00	
P	psia	0.45	14.7	453.0	0.0001	0.033	Aston et al. (4)
T	R	320.09	421.05	635.56	0.504	0.663	
P	psia	3.4	391.1	457.93	0.007	0.854	Mears et al. (98)
T	R	370.60	621.99	635.58	0.581	0.979	

*Critical constants of University of Michigan (136) are assumed when not available in the reference.

where P = pressure in psia

T = temperature in degrees Rankine

Equation II-17 predicted experimental data within an average deviation of 0.19% and maximum deviation of 0.44%.

Aston et al. (4), using 99.99% pure R-115 took eight vapor pressure data points which were correlated by the following equation

$$\log P = -\frac{1823.225}{T} - 11.51021 \log T + 0.007503762\,T + 36.185941 \qquad \text{(II-18)}$$

where P = pressure in mm of mercury

T = temperature in degrees Kelvin

Loffler and Matthias (87) took vapor pressure data for R-115 which is not available but was correlated by the following equation within an average deviation of ±0.02 atm.

$$\log (P/P_c) = -\frac{1530.38}{T} + 4.21313 - 4.58430 \log \left(\frac{T}{T_c}\right) + 0.120375 \left(\frac{T}{T_c}\right)^6 \qquad \text{(II-19)}$$

where P = pressure in atmospheres

T = temperature in degrees Kelvin (C + 273.15)

T_c = 353.15 K

P_c = 31.874

Mears et al. (98) obtained thirty-six experimental vapor pressure data points of 99.9 mole % pure R-115. Pressure measurements were precise to ±0.2% and temperature measurements to ±0.05%. The following vapor pressure equation was obtained.

$$\log P = A + \frac{B}{T} + CT + D \log T \qquad \text{(II-20)}$$

where P = pressure in atm.

T = temperature, K

$A = 3.8949764 \times 10^{1}$

$B = -1.9321347 \times 10^{3}$

$C = 1.0064705 \times 10^{-2}$

$D = -1.3949179 \times 10^{1}$

Eqn. II-20 agrees with data of Mears et al. (98) and Aston et al. (4) within average deviation of 0.33% and maximum deviation of 1.34%.

A-2(c) Saturated Liquid Density of R-115

Ranges of experimental saturated liquid density data are given in Table II-13.

Downing (41) reported two saturated liquid density data points for R-115 which were used in the correlations at The University of Michigan (136).

Using sealed tube method eight saturated liquid density measurements for R-115 were made at The University of Michigan (136). R-115 had an air composition of 0.0032% of vapor. Experimental data was correlated by the following equation.

$$d_s = 37.210 + 0.003648\,(t_c-t) + 1.1893\,(t_c-t)^{1/2} + 6.6857\,(t_c-t)^{3} + 2.8894 \times 10^{-5}\,(t_c-t)^{2} \qquad \text{(II-21)}$$

when d_s = density in lbs/cu.ft.

t = temperature in F

t_c = 175.89 F

TABLE II-13

RANGES OF SATURATED LIQUID DENSITY MEASUREMENTS FOR R-115

Property	Units	Minimum Value	Maximum Value	Critical Value*	Minimum Reduced Value	Maximum Reduced Value	Reference
ds	lbs/cu.ft.	75.63	90.46	37.20	2.033	2.432	Downing (41)
T**	R	561.64	470.38	635.56	0.883	0.74	
ds	lbs/cu.ft.	49.189	108.47	37.20	1.322	2.910	University of Michigan (136)
T**	R	632.50	316.46	635.56	0.995	0.498	
ds	lbs/cu.ft.	62.66	103.97	38.27	1.637	2.717	Mears et al. (98)
T**	R	613.38	355.34	635.58	0.964	0.558	

*Critical constant of University of Michigan (136) are assumed when not available
**Temperature values correspond to the density figures.

Equation II-21 represents the experimental liquid density values within an average deviation of 0.15%.

Loffler and Matthias (87) took some experimental measurements of saturated liquid density of R-115 which are not available but were correlated by the following equation

$$V = \frac{1.691}{1+0.79(1-\frac{T}{T_c} + 1.9414\ (1-\frac{T}{T_c})^{1/3}} \qquad \text{(II-22)}$$

where V = specific volume of saturated liquid, cm^3/g

T = temperature in K = C + 273.15

T_c = 353.15 K

Equation II-22 predicted their data within average deviation of ±0.3%.

Mears et al. (98) took 14 data points using 99.9% pure R-115. Volume measurements were precise to ±0.1 or better, temperature measurements ±0.05% or better and sample weight values ±0.05% or better. Experimental data was correlated by Martin-Hou equation (92) which is:

$$d_s = d_c + A(1-T_R)^{1/3} + B(1-T_R)^{2/3} + C(1-T_R) + D(1-T_R)^{4/3} \qquad \text{(II-23)}$$

where

d_s = saturated liquid density in g/cc

T_R = T/Tc

T_c = 353.1 K

d_c = 0.6131 g/cc

A = 1.5024

B = -2.0583

C = 4.0351

D = -2.0214

Equation II-23 predicts their experimental values with average deviation of 0.08% and maximum deviation of 0.25%.

A-2(d) Critical Constants of R-115

Table II-14 lists critical constants of R-115 as determined by different workers.

A-3 Physical Properties of R-502

Table II-15 lists works dealing with experimental determination of physical properties of R-502. Each work is discussed below.

A-3(a) PVT Behavior of R-502

No experimental data on PVT behavior of R-502 is available in the literature.

A-3(b) Vapor Pressure of R-502

Nineteen data points covering temperature range of -30 to 150 F were available from Downing (42) which were correlated by Badylkes (5,6, 7) using the following equation

$$\log_{10} P = A + B/(T/100) + C \log_{10} \left(\frac{T}{100}\right) - D \left(\frac{T}{100}\right)^6 \qquad \text{(II-24)}$$

where

P = vapor pressure in kg/cm^2 abs

T = temperature in K

A = +7.246308

B = -13.738168

C = -3.3686219

D = $-0.48709009 \times 10^{-4}$

TABLE II-14

CRITICAL CONSTANTS OF R-115

Critical Temp. R	Critical Pressure psia	Critical Volume ft^3/lb	Critical Density lb/ft^3	Critical Compressibility Factor	Reference
635.56	453.0	0.02687	37.20	0.2757	U. of M. (136)
635.67	468.42	0.02709	36.92	0.28736	Loffler and Matthias (87)
635.58	457.89	0.02613	38.25	0.2710	Mears et al. (98)

TABLE II-15

PHYSICAL PROPERTIES OF R-502

PVT Behavior	Vapor Pressure	Saturated Liquid Density	Critical Constants
None	1) Downing (1964)....(42)	1) Badylkes (1964)....(5,6,7)	1) Downing (1964)...(42)
	2) Badylkes (1964)....(5,6,7)	2) Loffler (1967)....(86)	2) Badylkes (1964)..(5,6,7)
	3) Loffler (1967)....(86)		3) Loffler (1967)...(86)

Equation II-21 predicted experimental data within a maximum deviation of 0.5%.

Loffler (86) measured vapor pressure of R-502 from -40 to +40 C and correlated it by the following equation

$$\ln\left(\frac{P}{P_c}\right) = -\frac{1449.7}{T} + 3.9609 + 0.1132\left(\frac{T}{T_c}\right)^6 - 1.7742\ln\left(\frac{T}{T_c}\right) \tag{II-25}$$

where P = pressure in atm.

T = temperature in degrees Kelvin

T_c = 355.85 K

P_c = 42 atm.

His experimental data which is not available, was predicted by Eqn. II-25 with average absolute deviation of 0.05 atm. and maximum deviation of 0.08 atm. This equation also predicts Badylke's (5,6,7) values with average absolute deviation of 0.015 atm. and maximum deviation of 0.05 atm. Compared with vapor pressure data from Du Pont Company (42) absolute average deviation of 0.038 atm. and maximum deviation of 0.16 atm. was found.

A-3(c) Saturated Liquid Density of R-502

Loffler (86) took saturated liquid density data for R-502 which is not available but was correlated by the following equation.

$$V_s = \frac{1.787}{1+0.85(1-T_R) + 1.902(1-T_R)^{1/3}} \tag{II-26}$$

where

V_s = specific volume of saturated liquid in cm /g

T_R = T/Tc

Tc = 355.85 K

Equation II-26 predicted his data within a maximum deviation of 0.3% and average absolute deviation of 0.2%. Estimated precision of experimental determinations was 0.3%. Eqn. II-26 predicted values calculated from corresponding states theory by Badylkes (5,6,7) within average absolute deviation of 0.9% and maximum deviation of 1.8%. Also values obtained from generalized correlations by Du Pont Company (47) were predicted by Eqn. II-26 within average absolute deviation of 1.6% and maximum deviation of 4.2%.

A-3(d) Critical Constants of R-502

Table II-16 lists critical constants of R-502 as reported by different investigators.

B. VARIABLE VOLUME EQUIPMENT FOR PVT MEASUREMENTS

History of PVT measurements goes back to about the 18th century. Ellington and Eakin (48) have published latest review of techniques of PVT measurements. High pressure techniques were reviewed by Bridgman (24). Ellington and Eakin (48) also reviewed constant volume method of PVT measurements.

Variable volume equipment may be classified into two sections:

1) Constant mass methods: mass of the test sample remains constant for a series of experiments.
2) Variable mass method: mass of the test sample changes in a series of experiments.

Constant mass methods are further divided into "wet" and "dry" methods depending on whether test sample comes in contact with a fluid during experimentation. Table II-17 lists works according to this classification.

TABLE II-16

CRITICAL CONSTANTS OF R-502

Critical Temp. R	Critical Pressure psia	Critical Volume ft^3/lb	Critical Density lb/ft^3	Critical Compressibility Factor	References
639.67	-	0.02875	34.80	-	Downing (42)
650.14	617.48	-	-	-	Badylkes (5,6,7)
640.53	617.4	0.02865	34.93	0.28729	Loffler (86)
639.56	591.0	0.2857	35.00	0.27465	This Work

TABLE II-17

VARIABLE VOLUME EQUIPMENT FOR PVT MEASUREMENTS

Constant Mass		Variable Mass
Wet Method	Dry Method	
I) Liquid Injected Piezometer	I) Cylinder-Piston	1) E.S. Burnett (1936) (27)
1) J. Canton (1762,1764) (30)	1) J. Perkins (1819,1820) (113)	
2) G. Aime' (1843) (1)	2) C.A. Parsons and S.S. Cook (1911) (110)	
3) L. Cailletet (1880) (28)	3) P.W. Bridgman (1923) (22)	
4) J.G. Tait (1881) (135)		
5) E.H. Amagat (1893) (2)	II) Bellows	
6) Carnazzi (1903) (31)	1) P.W. Bridgman (1931) (23)	
7) T.W. Richards (1903) (121)	2) R.K. Bhada (1968) (15)	
8) P.W. Bridgman (1913) (21)		
9) A. Michels and R.O. Gibson (1928) (100)		
10) F.G. Keyes (1933) (73)		

Burnett (27) first used variable mass and variable volume method for PVT measurements. Advantage of this method lies in non-requirement of mass balance which is sometimes a cause for major inaccuracies in PVT data. Since then many workers have used this method.

B-1(a) Constant Mass - Wet Method

History of PVT measurements goes back to the experiments of Canton (30). He proved water to be compressible by placing it in a large bulb connected to a capillary with a receiver of an air pump as a pressure generator. Changes in volume, however very small, were detected by observing meniscus of water in the capillary.

For high pressure measurements mercury was used as a pressure transmitting fluid. Glass piezometers surrounded by hydraulic fluid, mercury in most cases, were used. In this set up mercury level in the piezometer could not be observed. To overcome this difficulty Cailletet (28) gilded interior of the capillary. From the extent to which gilding was dissolved, position of mercury and consequently volume of the piezometer was determined. This procedure resulted in giving one reading at a time. Tait (135) used a floating hair index on top of the hydraulic fluid.

Inherent inefficiency in these one-reading methods was eliminated by Tait (135) using fused platinum contacts into the capillary. Volume of the piezometer corresponding to each platinum contact being well determined by a suitable calibration method, pressures for successive contacts of mercury with platinum wires were observed. This experimental set-up yielding multiple readings depending on the number of fused platinum contacts, used by other investigators (2,55,100,125). Amagat (2) used a similar set up to study compressibility of gases as well as liquids. Michels and Gibson (100) used an inverted glass buret of bulbs (Fig. II-3). Pressure to these bulbs is transmitted through mercury by hydraulic oil. Complete piezometer assembly was immersed in a temperature controlled bath. Pressure of the oil corresponding to each contact of mercury with platinum wire was recorded. Precision of the experimental data of Michels and Gibson (100) is of the order of 1:10,000. This equipment has been used to pressures as high as 3000 atmospheres. Detailed description of this equipment and experimental procedure is given by Schamp (125). Hagenbach and Coming (55) used bulbs of sequenced size in their buret. This Tait's type experimental set up cannot be used above 200 C since above this temperature mercury dissolves the platinum contacts. On the other hand precision in volume is of high magnitude even at pressures as high as 3000 atmospheres, because compressibility of glass enters into calculations of piezometer volume well above this pressure.

Carnazzi (31) designed slightly different equipment from that of Tait (135). He put a fine stretched wire along the bore of the capillary, whose electrical resistance can be measured. Electrical resistance of this wire varied according to the position of mercury in a capillary. However Carnazzi's method suffers from a drawback that capillary action is irregular thereby resulting into higher imprecision in volume than that obtained by the Tait method.

While Tait and Carnazzi's methods are multiple reading methods, Richards (121) devised a single reading method based on the same idea

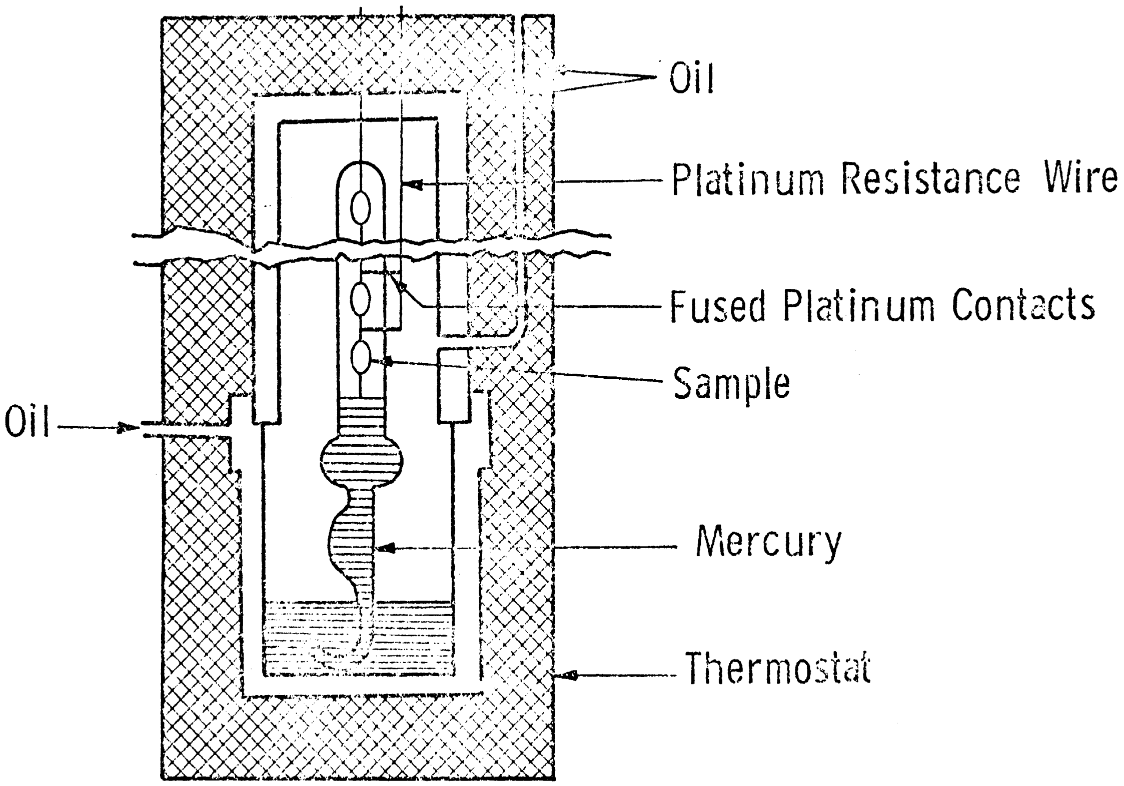

Fig. II.3. Michels' Variable Volume PVT Apparatus of contact of mercury with platinum. He joined a bulb to the capillary and fused a platinum contact at the junction. The bulb was set in an inverted position in a temperature controlled bath. A test fluid with a known amount of mercury would be filled in the bulb and pressure applied through hydraulic oil.

Pressure of the hydraulic oil corresponding to the mercury contact with platinum would be noted. The same procedure can be carried out with different amounts of mercury in the bulb. While the principle of changing volume of test sample by mercury remained the same, this method of Richards was a stepwise procedure, involving one reading for one cycle of pressurization and depressurization of the cell.

Methods of Tait, Carnazzi and Richards suffered from the disadvantage that due to dissolution of platinum wires in mercury, equipment could not be used above 200 C for PVT measurements.

Bridgman (21) used indirect piston displacement which Aime (1) employed in crude fashion. Bridgman (21) changed volume of the piezometer by forcing piston driven hydraulic fluid through a valve at the bottom of the piezometer. Volume of the piezometer was directly related to displacement of the piston. Aime (1) used hydrostatic pressure of sea water to force mercury into the piezometer and by weighing the amount of mercury forced, volume of the piezometer was determined. Knowing the compressibility of the hydraulic fluid and displacement of the piston, volume of the test sample was calculated by Bridgman (21). He used a manganin pressure gauge placed in the cylindrical bomb for high pressure measurements up to 9000 kg/cm^2. Similar equipment have been used by others (8,34,40,73). Complete description of the advanced equipment and experimental procedure is given by Keyes (73) and Beattie (8). This equipment is presented schematically in Fig. II-4. Douslin (40) using similar equipment, claims a precision of 3:10,000 for temperature near ambient and 3:1,000 at 300 C and 400 atmospheres.

There are other variations of the technique described above. Connoly and Kandalic (35) used a high strength glass capillary as a piezometer whose volume was calibrated. Pressure transmitting fluid was mercury and the volume of the capillary was determined by noting its unoccupied volume. This equipment was used to obtain low pressure PVT data on hydrocarbons to determine second virial coefficients. Precision of data was of the order of 3:10,000 around pressures of 10 atmospheres and 1:10,000 around pressures of 25 atmospheres. Doolittle et al. (39) used a stainless steel piezometer with mercury as the pressure transmitting fluid. An iron plug was placed on top of the mercury. Position of the column of mercury was determined by locating the iron plug using a differential transformer connected to a 1000 cycles/sec. bridge with a vacuum tube voltmeter as a null indicator. Volume measurements were claimed to be precise to 1:10,000 except around one atmosphere. Over all errors in density were estimated to be less than 4:10,000 up to pressures of 4000 kg/cm^2. Using an iron plug to locate the position of the mercury column made possible PVT measurements above 200 C.

The following classification may be made in summarizing these methods.

1. Platinum wire-mercury contact method
2. Indirect piston displacement method
3. Direct volume determination method.

B-1(b) Constant Mass - Dry Method

In this type of equipment the test sample does not come in contact with a fluid. The simplest equipment is a cylinder piston assembly which has a history of about 150 years. Bellows type equipment required advanced technology which was available around 1920. Both these types are discussed below.

I. Cylinder-Piston

As early as 1819, Perkins (113) used this method to measure compressibility of water. He used a cannon equipped with a movable plunger. Tolerance between the cannon and the sliding plunger was so small that no soft packing was needed. Cannon containing water as the test fluid was plunged into the sea at various depths using hydrostatic pressure of seawater as a pressure generator. The plunger was equipped with a sliding ring which was left at extreme positions thereby enabling to determine volume of water inside the cannon at respective pressures. Compressibility results obtained by this method were four times too small. Limitation of this experimental procedure was that only one reading could be obtained at a time. Parsons and Cook (110) also used this method. Later on, using advanced technology, Bridgman (21,22) built an apparatus to study compressibility of liquids at high pressures. Besides leak problems, he encountered rupturing of steel at high pressures. In the final analysis he writes (22), "I discard the method with regret, for its simplicity and directness." After his earlier relatively less successful attempts, Bridgman (24) in 1928 built a cylinder piston assembly (Fig. II-5) where he could obtain a fit between cylinder walls and piston of the order of 0.00001 inches.

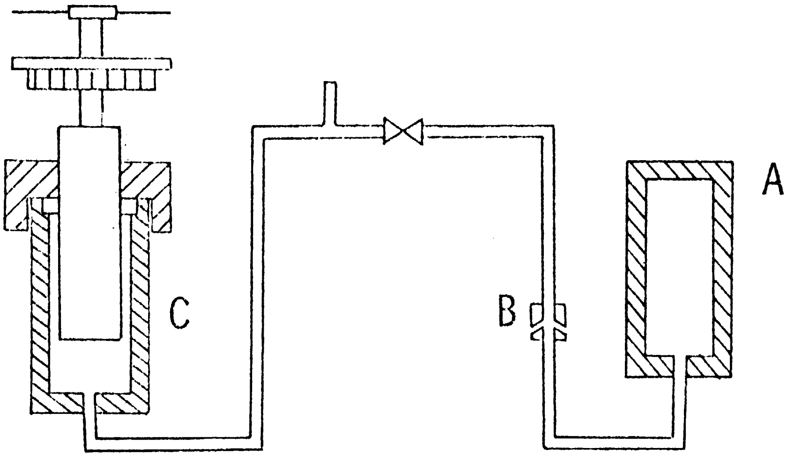

Fig II.4. Keyes and Beattie Equipment (8,73)

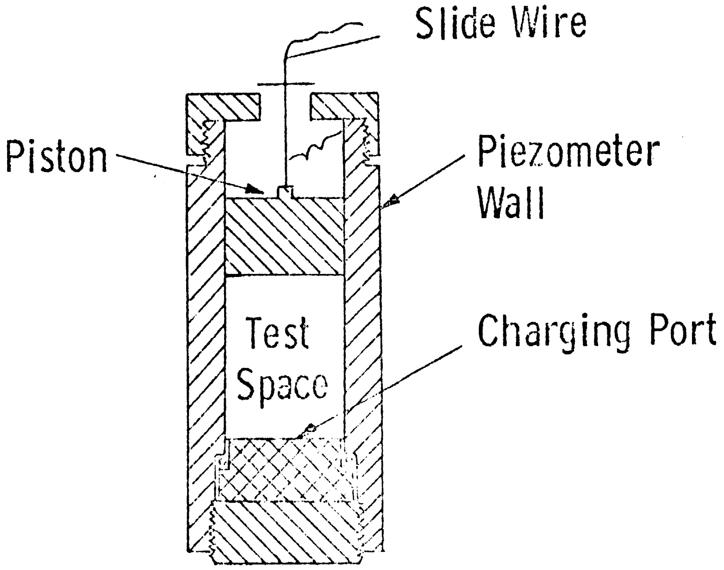

Fig. II. 5. Bridgman Piston Cell (24)

Position of the piston was determined by measuring resistance of a slide wire. Even such a well machined apparatus leaked due to uneven expansion of the cylinder with respect to the plunger at high temperatures.

B-1(b) Constant Mass - Dry Method

II. Bellows

As early as 1930, Bridgman (23) prepared brass bellows (Fig. II-6) to measure compressibility of liquids up to pressures of 12,000 kg/cm^2. Volume of the bellows was found by determining position of the top plate by the slide wire. The bellows was guided by a center post. In working with "Shim" brass, Bridgman (23) found that thickness of 0.002 inches was too large and that of 0.0012 inches too small in preparation of bellows. He eventually used 0.0015 inches (0.0038 cm) thick sheets in the manufacture of bellows. He also tried other materials of construction such as special grade brass recommended for deep drawing, phosphor bronze, nickel silver, soft iron, silver, platinum and copper. Bridgman (23) prepared his own bellows and has described his method of construction. The final form of bellows consisted of nine double sections with an unextended length of one inch. The bellows were flexible to the extent of 0.187 inches in both directions, giving 0.375 inches altogether or about 32% on the maximum volume. In his earlier attempts Bridgman (23) used an external guide for the bellows. Later on he introduced an internal guide. Total available volume of the bellows was about 5 cm^3. Absence of hysteresis was proved by obtaining pressure values in a complete cycle of pressurization and depressurization, which formed a smooth curve. Volume of the bellows was lineraly dependent on length of the bellows to better than 0.1%. Equipment was used in the temperature range of 0 to 95 C. Hysteresis effects due to temperature changes were within the experimental precision. Maximum temperature dependence of the constants of the apparatus amounted to a variation of 0.15%. Net maximum correction to isothermal values due to pressure effects was never more than 2% and that for the thermal expansion at constant pressures less than 6%. In his final analysis Bridgman (23) concluded that the bellows method was superior to his indirect-piston displacement method and undoubtedly the cylinder-piston method. Trade name of the bellows was "Sylphon".

Cutler et al. (38) used an apparatus similar to "Sylphon" to study compressibility of liquids between 35 to 135 C and pressures up to 10,000 bars. Estimated cumulative error in calibration constants was ±0.3%. Precision in volume was ±1.6% around 350 bars and ±0.4% around 10,000 bars. Precision in density was estimated to be about ±0.1% around 350 bars and about ±0.14% around 10,000 bars.

In 1968 Bhada (15) fabricated a stainless steel bellows capable of about 1000% volume change. The same equipment is used in this investigation and is described later.

B-2. Variable Mass

Errors in mass balance of a test sample are often the limiting errors in the precision of PVT data. Burnett (27) developed a method, based on the following equation, which does not require measurements of mass.

$$P_1 V_A = Z_1 n_1 R T \qquad \text{(II-27)}$$

The Burnett apparatus consists of two cells of volumes V_A and V_B immersed in a temperature controlled bath (Fig. II-7) connected by an expansion valve. In an experiment a sample is confined initially in the cell having V_A and after noting pressure P_1 at temperature T of the thermostat, it is allowed to expand into the cell having volume V_B, also at temperature T. Pressure P_2 is noted after expansion and then the expansion valve is shut off so that chamber B can be evacuated. For the total system volume of V_A and V_B after expansion we have:

$$P_2 \ (V_A + V_B) = Z_2 \ N_1 \ RT \tag{II-28}$$

On dividing Eqn. II-28 by II-27:

$$\frac{P_2}{P_1} \ \frac{(V_A + V_B)}{V_A} = \frac{Z_2}{Z_1} = \frac{P_2}{P_1} \ N \tag{II-29}$$

where N is an apparatus constant which depends only on volumes of two cells V_A and V_B. After a series of m successive expansions:

$$\left(\frac{P_{m+1}}{P_1}\right) N^m = \frac{Z_{m+1}}{Z_1} \tag{II-30}$$

or

$$P_{m+1} \ N^m = P_1 \ Z_{m+1}/Z_1$$

N, the apparatus constant, is a function of temperature and is determined as the limit of the ratio (P_m/P_{m-1}) as P_m goes to P_1. This task may be performed graphically or numerically by fitting an equation to the isothermal data.

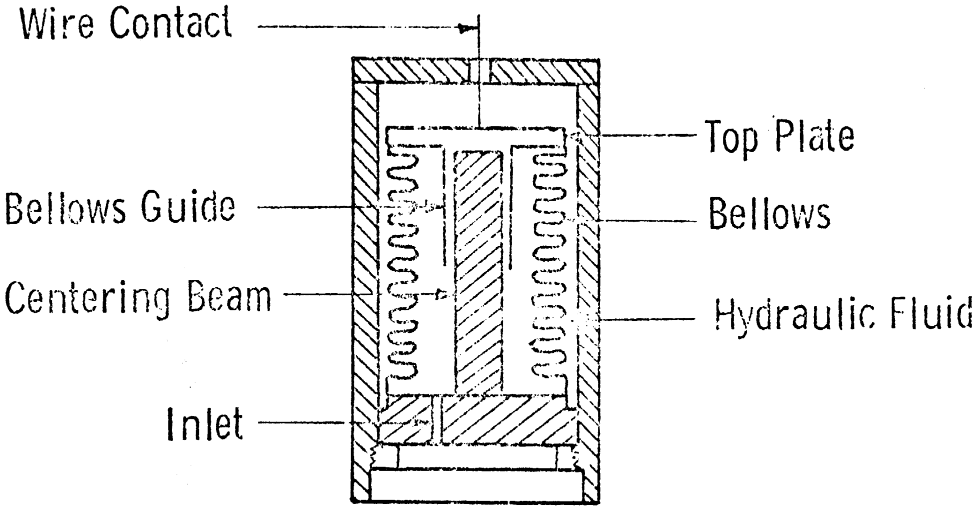

Fig II.6. Bridgman Bellows Cell (23)

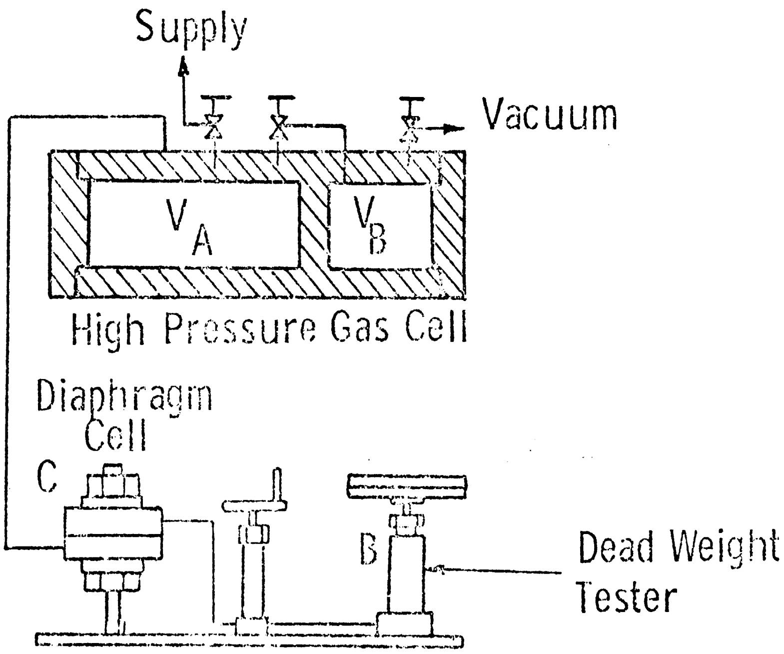

Fig II.7. Burnett Apparatus (27)

Burnett's procedure requires precise pressure measurements at low values unless the isotherm is linear to high pressures. Also any error in determination of the cell constant N, is magnified in the calculations of Z_{m+1} due to the fact that N is raised m times.

Schneider (126) used the Burnett apparatus for high temperature studies with a modification that the chambers A & B in Fig. II-7 were maintained at separate temperatures. Using Eqn. II-24 appropriately he was able to determine second virial coefficients to a precision of about 0.5% around 0 C and about 1% around 600 C.

Burnett apparatus has been described in detail by Bloomer (16), Mueller et al. (105) and Schneider (126). Experimental data processing has been described by Canfield (29), Pfefferle et al. (115) and Silberberg et al. (127). Estimated precision in Z was of the order of 2:1000 and in N, the cell constant, of the order of 1:10,000 according to Canfield (29).

C. INTERMOLECULAR POTENTIAL FUNCTIONS

A good representation of intermolecular potential energy is desirable for several reasons. On the molecular level, intermolecular distances are specified by the minimum in the potential energy; force constants for vibrating and rotating molecules are obtained from the second derivative of the potential energy with respect to intermolecular distance and higher derivatives determine anharmonicity constants.

A potential energy function may be used to calculate bulk properties like the second virial coefficient, the Joule-Thomson coefficient, coefficients of viscosity, thermal conductivity, self diffusion, the thermal diffusion factor in dilute gases and crystal properties at absolute zero. Several equations have been developed to fit bulk properties. In the following discussion we shall confine to the second virial coefficient, its relation to the intermolecular potential energy and various analytical expressions for the potential energy.

The second virial coefficient, denoted by B(T), is defined by the virial equation of state:

$$\frac{P\underline{V}}{RT} = 1 + \frac{B(T)}{\underline{V}} + \frac{C(T)}{\underline{V}^2} + \ldots \qquad \text{(II-27)}$$

where P = pressure of the substance under consideration

$\underline{V}$ = specific volume

R = gas constant

T = absolute temperature

B(T)= second virial coefficient

C(T)= third virial coefficient

Relationship between the second virial coefficient and the intermolecular potential energy, U(r), is derived through the use of statistical mechanics and is given by the following equation.

$$B(T) = \frac{-N}{4} \int_0^{\alpha} \int_0^{2\pi} \int_0^{\pi} \int_0^{\pi} [e^{-U/kT} - 1] \mathrm{Sin}\theta_1 \, d\theta_1 \, \mathrm{Sin}\theta_2 d\theta_2 d(\theta_2 - \theta_1) r^2 dr \qquad \text{(II-28)}$$

where $B(T)$ = second virial coefficient

U = intermolecular potential energy

k = Boltzman constant

T = absolute temperature

θ_1, θ_2 = polar angles

ϕ_1, ϕ_2 = azimuthal angles

r = intermolecular distance

N = Avagadro number

Some general observations suggest the nature of the potential energy curve. The phenomenon of gases condensing to liquids, indicates that at large separations, the forces must be attractive. At the same time the effect that liquids resist compression suggests that the forces at small separations must be repulsive. Therefore the potential energy between two molecules will vary with respect to the separation distance as shown in Fig. II-8.

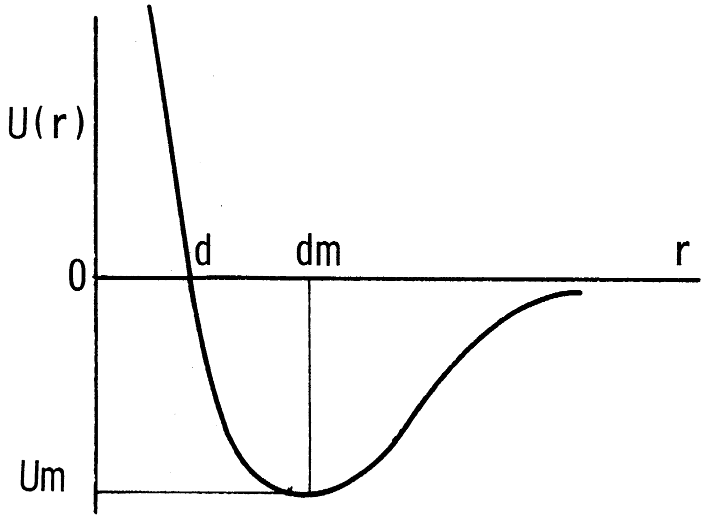

Fig. II-8. General Representation of the Intermolecular Potential Energy

Next we must consider the shape and nature of the interacting molecules. As a simple case, let us consider the two molecules which are spherically symmetric in shape and the electronic charge distribution (Fig. II-9).

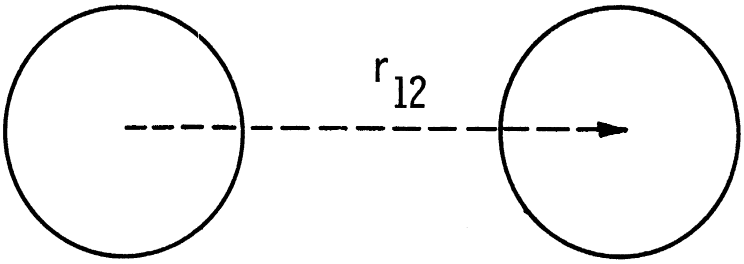

Fig. II-9. Interaction Between Spherically Symmetric Molecules

In this case, the center of force may be assumed to coincide with their geometric centers and then the potential energy U_{12} is simply a function of r_{12}. The integration in the Eqn. II-28 over the orientation angles can be performed for this case resulting into the following expression.

$$B(T) = -2\pi N \int_0^\infty (e^{-U_{12}/RT} - 1)\, r_{12}^2\, dr_{12} \tag{II-29}$$

The significance of the symbols is described for the Eqn. II-28.

As a little more difficult case, let us consider the two molecules, each having two centers of forces as in Fig. II-10.

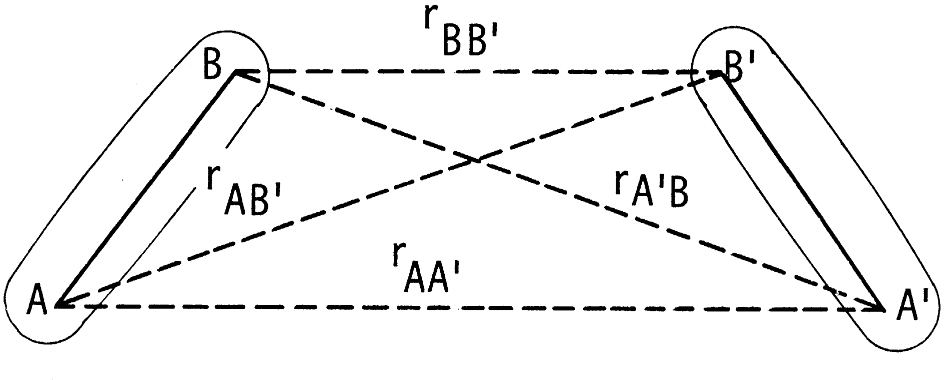

Fig. II-10. Interaction Between Molecules Having Two Centers of Forces

The total potential energy is calculated by the rule of pairwise additivity of the individual pair potential energies. Since the distances r_{AA}' , r_{AB}', etc. are functions of orientations of both molecules, the intermolecular potential energy U_{12} has angular dependence. Integration in the Eqn. II-28 is very involved in this case.

The case of molecules possessing dipole moments is a particular variation of the case of molecules of two centers of forces (Fig. II-11).

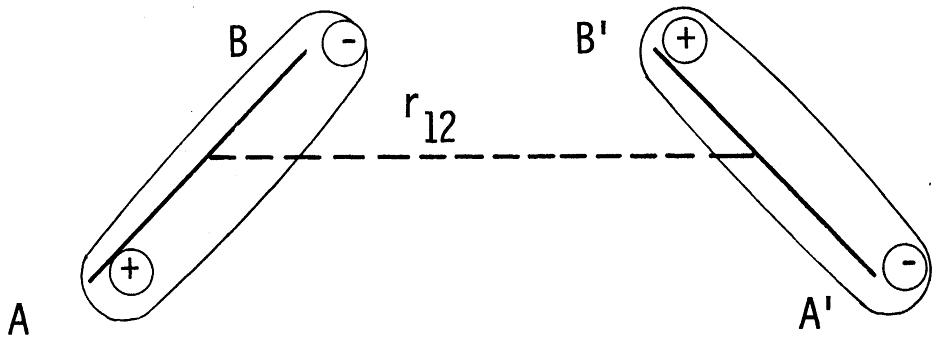

Fig. II-11. Interaction Between Molecules Possessing Dipole Moments

The potential energy between the dipoles then depends on the dipole moments, the distance r_{12} as shown in Fig. II-11 and orientation of both molecules.

Similar qualitative picture can be obtained for complex cases of molecules possessing more than two centers of forces.

The two molecules are considered totally interpenetrable if, at the least, their centers coincide completely resulting into zero intermolecular separation. Realistically no molecule is totally interpenetrable and partial penetrability can be assumed to be a rule. In such a case, the molecule is considered as having a hard core surrounded by a soft core. This is presented in Fig. II-12.

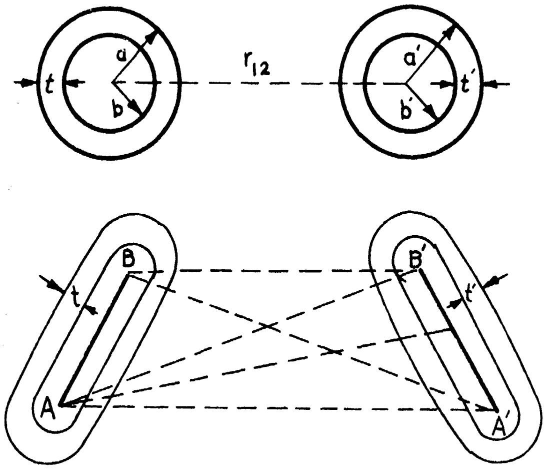

Fig. II-12. Interaction Between Partially Penetrable Molecules

The potential energy now depends on an additional factor, the thickness, t, of the penetrable shell of the molecule.

INTERMOLECULAR FORCES

Intermolecular forces are arbitrarily divided into two categories as short range forces, and long range forces. Short range forces, frequently termed valence forces or chemical forces, arise due to overlapping of electron clouds of two molecules. These forces are highly repulsive. Calculations of these short range forces are based on quantum mechanics and are very complicated. Only simple systems like H_2+, H_2 have been treated.

Long range forces are generally considered to be made up of three parts: 1) electrostatic interaction, 2) interaction due to induction, and 3) dispersion forces. In the following discussion we shall summarize the results and the detailed treatment of these forces is given elsewhere (58,69).

ELECTROSTATIC CONTRIBUTION

Various multipole interactions contribute to the total intermolecular potential energy. Coulombic law of electrostatic interaction gives formulae for various types of interactions.

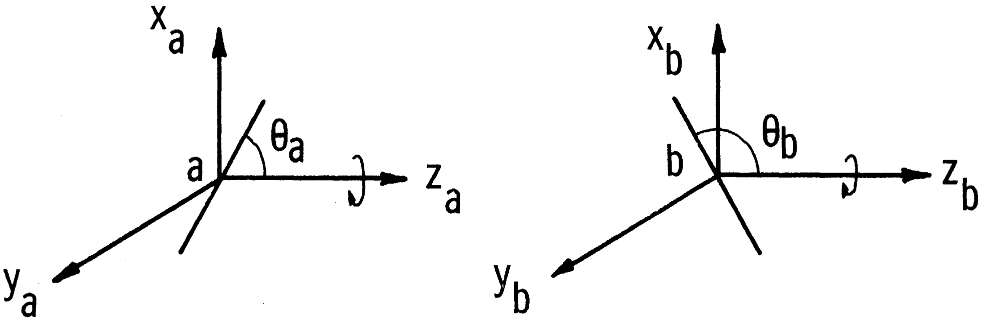

Fig. II-13. Electrostatic Interaction Between Two Molecules

With relation to Fig. II-13 the interactions are as follows:

$$Uab^{(C,C)} = +\frac{C_a C_b}{r} \qquad \text{(II-30a)}$$

$$Uab^{(C,\mu)} = -\frac{c_a \mu_b \, \mathrm{Cos}\theta_b}{r^2} \qquad \text{(II-30b)}$$

$$Uab^{(C,Q)} = +\frac{C_a Q_b}{4r^3}\,(3\mathrm{Cos}^2\theta_b - 1) \qquad \text{(II-30c)}$$

$$Uab^{(\mu,\mu)} = -\frac{{}_a\,{}_b}{r^3}\,[2\mathrm{Cos}\theta_a \mathrm{Cos}\theta_b - \mathrm{Sin}\theta_a \mathrm{Sin}\theta_b \mathrm{Cos}(\phi_a - \phi_b)]$$

where $Uab^{(C,C)}$ = energy of interaction between molecule a and molecule b, both possessing charges C_a and C_b, respectively

C_a, C_b = charge of the molecule

μ_a, μ_b = dipole moment of the molecule

Q_b = quadrupole moment of the molecule b

θ_a, θ_b = polar angles

ϕ_a, ϕ_b = azimuthel angles

The average potential energy $\bar{U}ab$ is obtained by averaging Uab over all angles with the use of Boltzman weighting factor exp.(-Uab/kT). For specifically symmetric potential functions the potential energy is given by the following expression.

$$\bar{U}ab = \frac{\iint Uab\ e^{-Uab/kT}\ d\omega a d\omega b}{\int e^{\bar{\ }Uab/kT}\ d\omega a d\omega b} \qquad \text{(II-31)}$$

where $d\omega = \mathrm{Sin}\theta d\theta d\theta$

Boltzman factor accounts for the assumption that statistically molecules spend more time in those orientations for which the energy is minimum.

For the dipole-dipole interaction given in Eqn. II-30d, average intermolecular potential energy for large separations is:

$$\bar{U}ab^{(\mu,\mu)} = -\frac{2}{3kT}\ \frac{\mu_a{}^2\mu_b{}^2}{r^6} \qquad \text{(II-32)}$$

where symbols are explained in Eqn. II-30.

Dipoles considered in Eqn. II-32 are ideal and the treatment of real dipoles is given by Hirschfelder, Curtiss and Bird (58).

INDUCTION CONTRIBUTION

With respect to Fig. II-14, let us consider charged particle 'a' inducing dipole moment in a neutral molecule 'b' resulting into induction interaction.

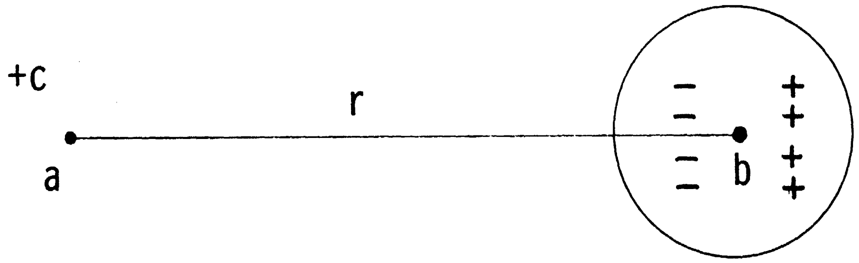

Fig. II-14. Induction Interaction Between Two Molecules

If 'a' possesses dipole moment μ_a, then the interaction between this dipole and the induced dipole is:

$$\mathrm{Uab}^{(\mu,\mathrm{ind}\mu)} = -\frac{\mu_a 2\ b(3\mathrm{Cos}^2\theta_a+1)}{2r^6} \qquad \text{(II-33)}$$

where αb = polarizability of the molecule b

θa = polar angle

Substituting this into Eqn. II-31, we obtain the average potential energy as:

$$\bar{\mathrm{U}}\mathrm{ab}^{(\mu,\mathrm{ind}\ \mu)} = -\frac{\mu_a^2 \alpha b}{r^6} \qquad \text{(II-34)}$$

For cylindrically symmetric molecules the induction contribution to the potential energy is (58) as follows:

$$\bar{\mathrm{U}}\mathrm{ab} = -\frac{1}{2}\,\alpha b\,[\frac{\mathrm{Ca}^2}{r^4} + \frac{2\mu a^2}{r^6} + \frac{3\theta a^2}{r^8} + \ldots] - \frac{1}{2}\,\alpha a\,[\frac{\mathrm{Cb}^2}{r^4} + \frac{2\mu b^2}{r^6} + \frac{3\theta b^2}{r^8} + \ldots] \qquad \text{(II-35)}$$

where Ca, Cb = charge of the molecule

αa, αb = polarizability of the molecule

μa, μb = dipole moment of the molecule

θa, θb = quadrupole moment of the molecule

DISPERSION CONTRIBUTION

For spherically symmetric molecules, the dispersion energy is independent of the orientation of the molecules and is given by the following equation.

$$U_{ab}^{dis} = -\frac{C}{r^6} - \frac{C'}{r^8} - \frac{C''}{r^{10}} \qquad \text{(II-36)}$$

where U_{ab}^{dis} = dispersion energy between molecules a and b

C, C', C'' = constants

r = intermolecular distance

First term in Eqn. II-36 is associated with interaction between two mutually induced dipoles and the constant C is given as:

$$C = -\frac{3}{2}\,\frac{E_{Ia}E_{Ib}\alpha a\alpha b}{2(E_{Ia}+E_{Ib})} \qquad \text{(II-37)}$$

where $E_{Ia}E_{Ib}$ = empirical constants which are often approximated to equal to ionization energy of the respective molecule.

Other terms in the Eqn. II-36 describe interactions between higher induced moments. For asymmetrical molecules dispersion interaction depends on orientations (58).

In summarizing the discussion on potential energy of interaction between two spherically symmetric polar molecules (58), for slightly polar molecules dispersion contribution amounts to about 99.9% and the rest is made up of electrostatic and induction contributions. For highly polar molecules, electrostatic contribution amounts to about 76%, dispersion contribution is about 20% and balance is made up by induction contribution.

For spherically symmetric non-polar molecules, long range forces arise totally due to dispersion effects and intermolecular potential energy is inversely proportional to sixth power of intermolecular separation. Asymmetric molecules show the same dependence on intermolecular distance.

SECOND VIRIAL COEFFICIENT FOR MIXTURES

Statistical mechanics gives a quadratic relationship between the second virial coefficient for mixture and its components as:

$$B_{mix} = \sum_{i=1}^{m} \sum_{j=1}^{m} Y_i \, Y_j \, B_{ij} \qquad \text{(II-38)}$$

where B_{mix} = mixture second virial coefficient

Y_i, Y_j = mole fraction of ith and jth component

m = total number of components

$B_{ij} (i=j)$ = second virial coefficient of interaction between molecules of ith and jth component

There are a few ways of calculating the second virial coefficient of a mixture. Usually the second virial coefficients for like molecules, B_{ii}, are available through the experiment or can be calculated if the intermolecular potential energy parameters are known. Then the problem of evaluating the second virial coefficient for unlike molecules, B_{ij}, is solved through averaging procedures such as follows:

$$B_{ij} = (B_{ii} + B_{jj})/2 \qquad \text{(II-39)}$$

Alternately, potential energy parameters can be used strictly to obtain B_{mix}. For the sake of example let us consider a two parameter potential energy function such as Lennard-Jones (12-6) (85). The parameters are U_m and d_m. Therefore starting with these parameters for pure components, we can obtain corresponding second virial coefficients using Eqn. II-29. Now the pure component parameters can be averaged to obtain interaction parameters using such rules as follows:

$$d_{mij} = \frac{1}{2} (d_{ii} + d_{jj}) \tag{II-40}$$

$$U_{mij} = (U_{mii} \times U_{mjj})^{1/2} \tag{II-41}$$

These averaged parameters are used to obtain interaction virial coefficients B_{ij} and using all this information, B_{mix} can be evaluated from the Eqn. II-38.

Thus mixture second virial coefficients can be calculated strictly from molecular parameters or from experimental component second virial coefficients.

INTERMOLECULAR POTENTIAL FUNCTIONS

The latest review of equations representing intermolecular potential energy is given by Fitts (50). Other excellent treatise is that of Hirschfelder, Curtiss and Bird (58). Varshni (137) reviewed potential energy functions for diatomic molecules. Mason and Spurling (95) have given another thorough treatment on this subject.

Following is a compilation on the analytical equations for potential energy. On several occasions the analytical expression cannot be integrated in Eqn. II-29, but with the use of fast electronic computers numerical integrations can be carried out. Wherever possible the final analytical expression for B(T) is given. The analytical equations are broadly classified into two categories as angle independent and angle dependent expressions. Angle dependency may be due to shape or the charge distribution. Altogether twenty potentials are discussed below.

I. Angle-Independent Analytical Equations for Intermolecular Potential Energy

1. Hard Spheres Model: The molecules in this model are assumed to be perfectly rigid spheres with no interaction at large separations and infinite force of repulsion when they touch each other as shown in Fig. II-15. Mathematically this interaction is described as follows:

$$U(r) = \infty \quad \text{for } r \leq d \qquad \text{(II-42)}$$

$$U(r) = 0 \quad \text{for } r > d$$

where d = diameter of the molecules

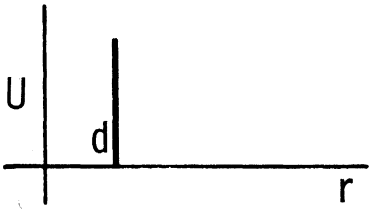

Fig. II-15. Hard Sphere Interaction

The second virial coefficient for this model is given by the following equation:

$$B = \frac{2}{3}\pi N d^3 \qquad \text{(II-43)}$$

The second virial coefficient as expressed in Eqn. II-43 is independent of temperature and is always positive resulting into compressibility factor greater than unity. These two qualities of B for the hard sphere model are not in accord with the facts.

2. <u>Point Centers of Repulsion</u>: In this model interaction between two molecules is assumed to be of a repulsive nature at all intermolecular separations as shown in Fig. II-16. The analytical expression for this interaction is as follows:

$$U(r) = ar^{-c} \tag{II-44}$$

where a = constant

c = index of repulsion

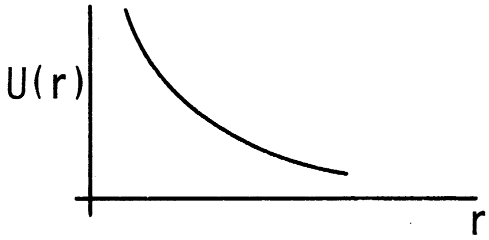

Fig. II-16. Interaction for Point Centers of Repulsion

The value of c is usually taken between nine and 15. On inserting Equation II-44 in Equation II-29, we obtain the second virial coefficient as follows:

$$B(T) = \frac{2}{3}\pi N \left(\frac{a}{kT}\right)^{3/c} \Gamma\left(\frac{c-3}{c}\right) \tag{II-45}$$

providing $c > 3$

Here B(T) is a function of temperature but it is not correct since it is positive for all temperatures.

3. <u>The Sutherland Model</u>: This model assumes the interaction to be an attractive for separations larger than the diameter of the molecules and infinitely repulsive for smaller separations as shown in Fig. II-17. The intermolecular potential energy is given by the following equation:

$$\begin{aligned} U(r) &= \infty \quad \text{for } r < d \\ &= \frac{-a}{r^b} \quad \text{for } r > d \end{aligned} \tag{II-46}$$

where a = parameter

b = index of attraction

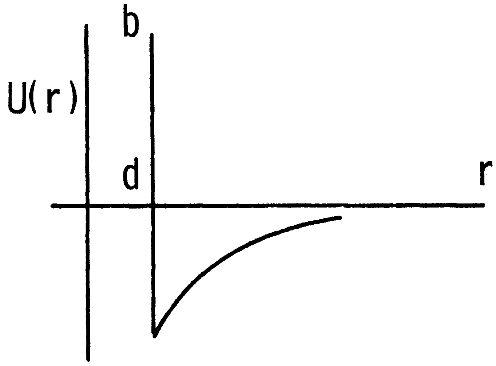

Fig. II-17. The Sutherland Model

The index of attraction, b, is taken as 6 to be consistent with London's Theory of dispersion forces. Using Equation II-46 in Equation II-29, the second virial coefficient is given by the following equation:

$$B(T) = -\frac{2\pi N d^3}{3} \sum_{j=0}^{\infty} \frac{1}{j!} \left(\frac{3}{6j-3}\right) \left(\frac{a}{d^6 kT}\right)^j \tag{II-47}$$

Eqn. II-47 involves two parameters d and a which can be determined from two values of B(T). This model correctly gives negative B at low temperatures and a constant positive value at high temperatures which is approximately in accord with the facts.

4. Lennard-Jones 12-6 Potential: Mie (103) first suggested that U(r) may be expressed as the sum of two terms, a negative term proportional to r^{-m} and a positive term proportional to r^{-n} with n > m > o. Lennard Jones assigned the values of n=12 and m=6 giving the following expression:

$$U(r) = 4Um \left[\left(\frac{d}{r}\right)^{12} - \left(\frac{d}{r}\right)^{6} \right] \qquad \text{(II-48)}$$

where various symbols are shown in Fig. II-18.

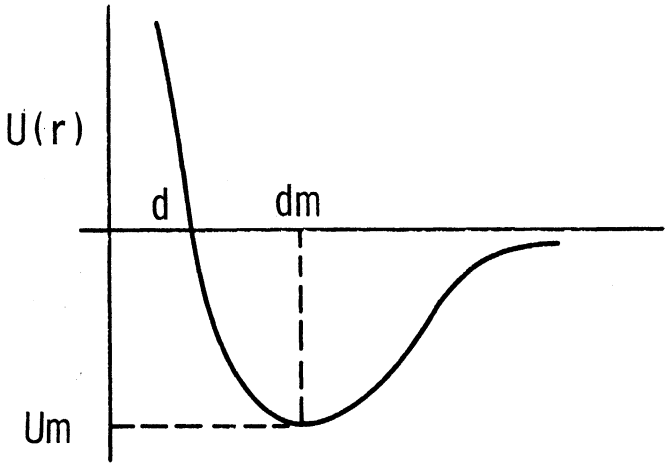

Fig. II-18. Lennard-Jones 12-6 Potential

The minimum in energy, Um, occurs at dm. Substituting for U(r) from Eqn. II-48 in the equation II-29, the second virial coefficient is given as follows:

$$B(T) = \frac{2}{3}\pi N d^3 \sum_{j=0}^{\infty} \left(\frac{kT}{Um}\right)^{-(2j+1)/4} \frac{-(2j+1)/2}{4j!} \Gamma\left(\frac{2j-1}{4}\right) \qquad \text{(II-49)}$$

As can be seen, there are two parameters d and Um in this potential which can be evaluated by two values of B(T). The results fit the experimental second virial coefficient fairly well over wide ranges of temperature. The dimensionless second virial B*(T*) and dimensionless temperature T* are defined as follows.

$$T^* = kT/Um$$

and $$B^*(T^*) = B(T)/(2/3\pi N d^3) \qquad \text{(II-50)}$$

Tables of B* as a function of T* are given by Hirschfelder, Curtiss and Bird (58) along with values of d and Um for several substances.

5. <u>Dymond, Rigby and Smith Potential</u>: The intermolecular potential energy as proposed by Dymond, Rigby and Smith (44) is given by the following equation:

$$U(r) = Um\,[0.331\,(\frac{d}{r})^{28} - 1.2584\,(\frac{d}{r})^{24} + 2.07151\,(\frac{d}{r})^{18} - 1.74452\,(\frac{d}{r})^{8} - 0.39959\,(\frac{d}{r})^{6}] \qquad \text{(II-51)}$$

where d and Um have the same significance as that for Lennard-Jones potential (Fig. II-18). The difference between this potential and the Lennard-Jones potential is given in Fig. II-19.

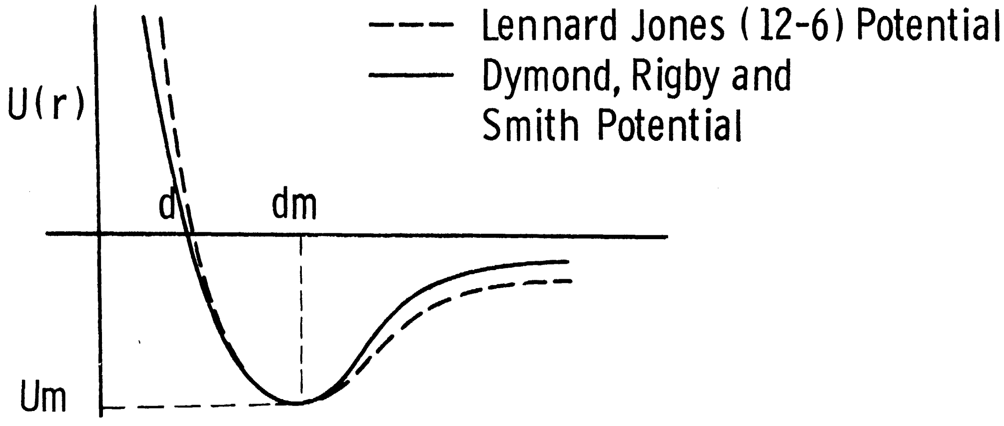

Fig. II-19. Dymond, Rigby and Smith Potential

It may be observed from Fig. II-19 that this potential has a broader bowl than that for Lennard-Jones (12-6) potential. Using equation II-51 in Equation II-29, integration is done numerically and results are given in the form of tables of B* as a function of T* (both quantities defined in Equation II-50) by Dymond, Rigby and Smith (44). The procedure to evaluate molecular parameters Um and d is the same as that used for calculating the parameters for Lennard-Jones (12-6) potential. The authors list molecular parameters for several substances.

6. Guggenheim and McGlashan: Using crystal data, Guggenheim and McGlashan (53) developed the intermolecular potential for argon which is given by the following equation:

$$
\begin{aligned}
U(r) &= \infty && \text{for } r \leq d \\
&= -Um + a\left(\frac{r-dm}{dm}\right)^2 - b\left(\frac{r-dm}{dm}\right)^3 + c\left(\frac{r-dm}{dm}\right)^4 && \qquad (\text{II-52}) \\
& && \text{for } 3.6A^0 \leq r \leq 4.15A^0 \\
&= -1\left(\frac{d}{r}\right)^6 && \text{for } r \geq 5.4A^0
\end{aligned}
$$

where Um, 1, a, b and dm are five characteristic constants and c is taken to be equal to b. This potential is a discontinuous one and in those regions ($d \leq r \leq 3.6A^0$ and $4.15 \leq r \leq 5.4A^0$) the potential curve is made continuous by free hand drawing. The authors selected 1 in order to agree with the theoretical dispersion force constant. Other parameters Um, a, b and dm were determined from crystal properties while d was evaluated from the second virial coefficient data. The second virial coefficient for this potential is evaluated by graphical integration. This potential predicts B for Argon at low temperatures to a high degree of accuracy but fails at high temperatures since repulsive energy is not in accord with the facts. Fender and Halsey (49) found that this potential fitted their low temperature second virial coefficients for Argon within 1%. The authors (54) applied their potential to Kr and Xe for which second virial data of Fender and Halsey (49) was used.

7. Square-Well Potential: In this model molecules are assumed to have a rigid core surrounded by a purely attractive core. The resulting potential is given in Fig. II-20 and expressed by the following equation:

$$
\begin{aligned}
U(r) &= \infty && \text{for } r < d \\
&= -Um && \text{for } d < r < \alpha d \\
&= 0 && \text{for } d > \alpha d
\end{aligned}
\qquad \text{(II-53)}
$$

where the symbols are explained in Fig. II-20.

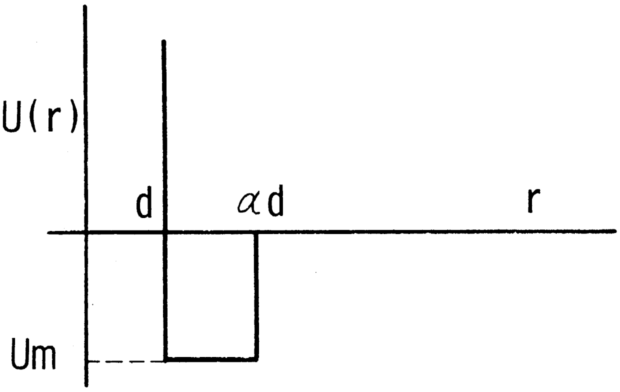

Fig. II-20. Square-Well Potential

Equation II-53 involves three parameters namely Um, d and α. Using Equation II-53 in the equation II-29, the second virial coefficient is given as follows:

$$B(T) = \frac{2}{3}\pi N d^3 \left[1 - (\alpha^3 - 1)\left(e^{Um/kT} - 1\right)\right] \tag{II-54}$$

The three parameters can be evaluated from three values of B(T). This potential has no interpenetration of molecules and therefore the values of B at high temperature are not in accord with the facts. Since there are three parameters, this potential predicts B for complex molecules better than two parameter potentials. The molecular parameters for this potential for several substances are compiled by Hirschfelder, Curtiss and Bird (58).

8. The Buckingham-Corner Potential: Buckingham (25) proposed a potential having exponential repulsion term and attractive portion made up of two terms. This potential is presented in Fig. II-21 and given by the following equation:

$$U(r) = be^{-ar} - cr^{-6} - c'r^{-8} \tag{II-55}$$

where a, b, c and c' are parameters.

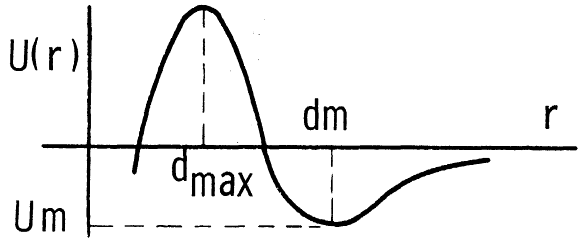

Fig. II-21. Buckingham Potential

The potential energy goes through a maximum at separation less than dm (where potential energy is minimum) and goes to negative infinity as zero separation approaches. Since this behavior of the potential does not compare with the facts, Buckingham and Corner (26) modified this potential and the result is presented in Fig. II-22. The modified equation is as follows:

$$U(r) = b \exp. \left[- \alpha\left(\frac{r}{dm}\right)\right] - (cr^{-6} - c'r^{-8}) \exp \left[-4\left(\frac{dm-1}{r}\right)^3\right] \quad \text{for } r \leq dm \qquad \text{(II-56a)}$$

$$= b \exp \left[- \alpha\left(\frac{r}{dm}\right)\right] - (cr^{-6} + c'r^{-8}) \quad \text{for } r \geq dm \qquad \text{(II-56b)}$$

where

$$b = [- Um + (1+B)\ Cdm^{-6}]\ e^{\alpha} \qquad \text{(II-57a)}$$

$$c = Um\alpha dm^6/[\alpha(1+B)-6-8B] \qquad \text{(II-57b)}$$

$$c' = Bd^2mC \qquad \text{(II-57c)}$$

$$B = c'dm^{-8}/cdm^{-6} \qquad \text{(II-57d)}$$

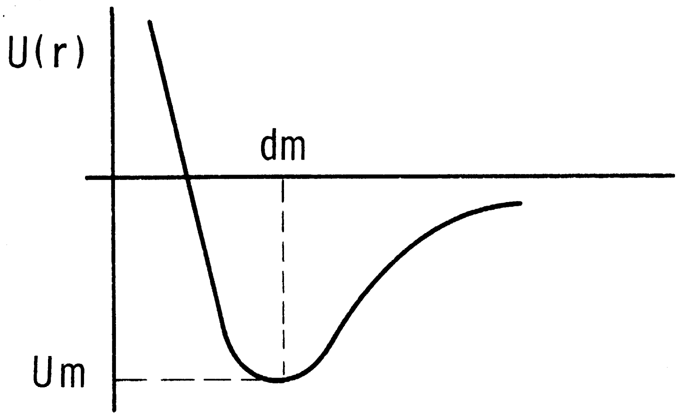

Fig. II-22. Buckingham-Corner Potential

This potential function has four parameters Um, dm, α, and B. Parameter α determines the steepness of the exponential repulsion and is usually taken as 13.5. The second virial coefficient B(T) is tabulated as a function of F, (58), where the relationship between B(T) and F is given by the following equation:

$$B(T) = 2\pi N d^3 m F\ (\alpha,\ B,\ \frac{kT}{Um}) \qquad \text{(II-58)}$$

The molecular parameters for some noble gases are given by Hirschfelder, Curtiss and Bird (58).

9. Exp-6 Potential: Buckingham potential (Eqn. II-55) was modified to give the Exp-6 potential which is presented in Fig. II-23 and expressed as follows:

$$U(r) = \frac{Um}{1-6/\alpha}\ [\frac{6}{\ }\ \exp\ (\alpha[\ 1 - \frac{r}{dm}])\ - (\frac{dm}{r})^6\ ] \quad \text{for } r \geq d_{max} \qquad \text{(II-59)}$$

$$= \infty$$

$$= \infty \qquad \text{for } r \leq dmax$$

where dmax is the separation at which potential is maximum in the Eqn. II-55.

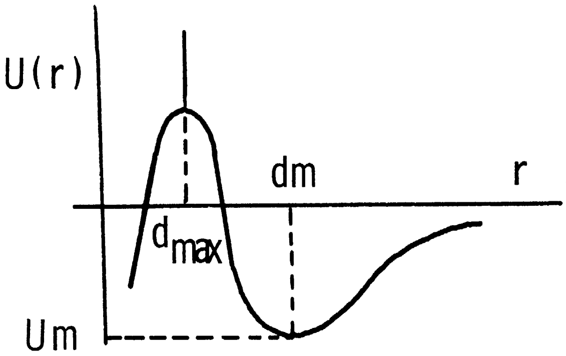

Fig. II-23. Exp-6 Potential

This potential contains three parameters: Um, dm and α. Steepness of the repulsive section is given by α. Using Eqn. II-59 in Eqn. II-29, we obtain the second virial coefficient as:

$$B(T) = \frac{2}{3}\pi N d^3 m F\ (\alpha, \frac{kT}{Um}) \qquad \text{(II-60)}$$

The function F is tabulated by Hirschfelder, Curtiss and Bird (58), who have also compiled the values of the molecular parameters of this potential for several substances.

10. <u>Carrà and Konowalow Potential</u>: The exp-6 potential was further improved by Carrà and Konowalow (32). This potential is presented in Fig. II-24 and expressed as follows:

$$U(r) = Um\ (\frac{\alpha+6}{\alpha})\ (\frac{dm}{r})^6\ [\frac{\alpha}{\alpha+6} \exp\ (\ [1 - \frac{r}{dm}]) - 1] \qquad \text{(II-61)}$$

where Um, α and dm have the same significance as that given in the original Buckingham potential (Eqn. II-55).

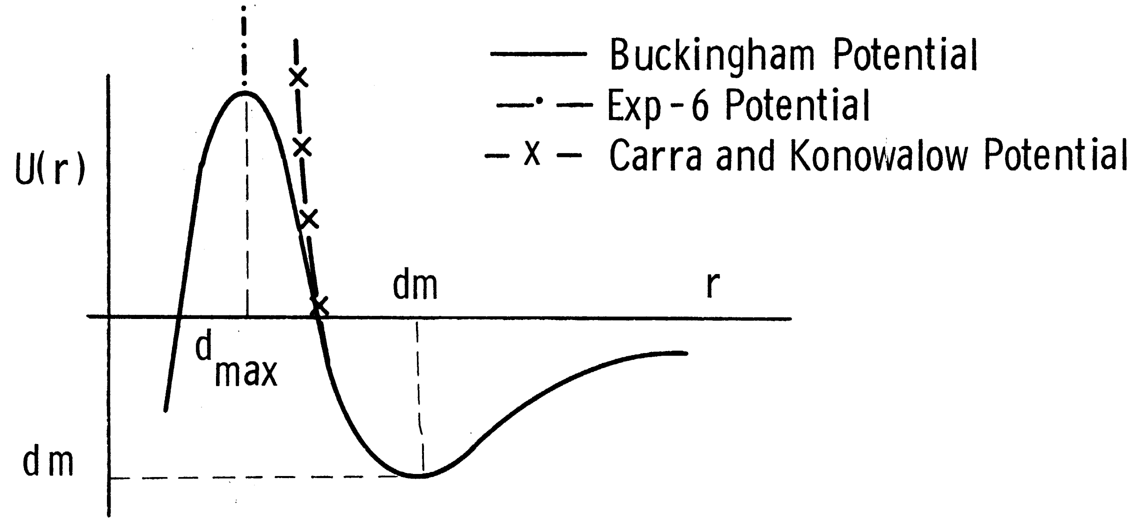

Fig. II-24. Carrà and Konowalow Potential

This potential is sometimes referred to as the Buckingham-Carrà-Konowalow (BCK) potential. The three characteristic molecular parameters are Um, α and dm. The second virial coefficient is obtained by using Eqn. II-29 in conjunction with II-61 to give the following relationship:

$$B(T) = \frac{2}{3}\pi N d^3 m F\left(\alpha, \frac{kT}{Um}\right) \qquad \text{(II-62)}$$

where F for this potential is tabulated in Ref. 58. The molecular parameters of this potential for several substances are obtained by Main and Saxena (108).

11. Modified Buckingham-Carrà-Konowalow Potential: Nain and Saksena (107) assumed a rigid spherical core inside a molecule and extended BCK potential to this molecular interaction. This potential is presented in Fig. II-25 and expressed mathematically as follows:

$$U(r) = Um \left(\frac{\alpha+6}{\alpha}\right) \left(\frac{dm-adm}{r-adm}\right)^6 \left\{ \frac{6}{\alpha+6} \left[\alpha\left(1- \frac{r-adm}{dm-adm}\right)\right] -1\right\} \qquad \text{(II-63)}$$

where parameter a is the ratio of core diameter to dm.

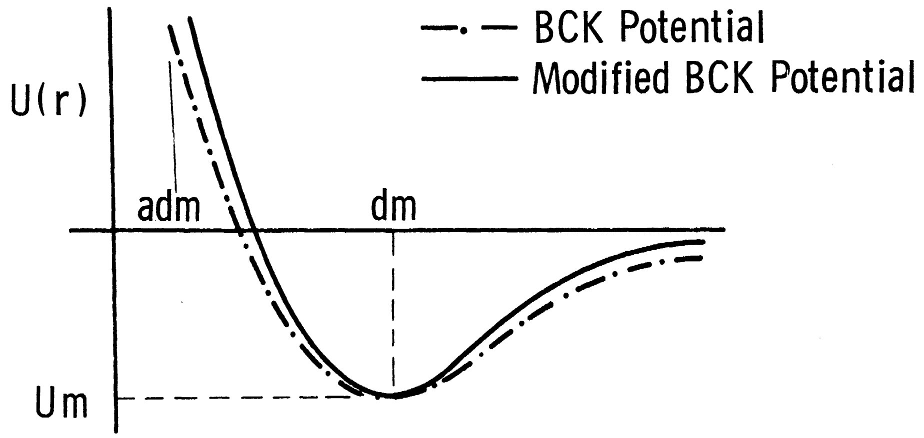

Fig. II-25. Modified Buckingham-Carrà-Konowalow Potential

Eqn. II-63 involves four parameters namely Um, dm, α and a. No second virial coefficient calculations have yet been made for this potential.

12. Morse Potential: Morse (104) proposed a potential in which both attractive and repulsive terms are exponential. The potential is presented in Fig. II-26 and mathematically expressed as follows:

$$U(r) = Um \{ \exp [- \frac{2c}{do}(r-dm)-2 \exp [- \frac{c}{do}(r-dm)] \quad (II-64)$$

where $\frac{dm}{d} = 1+\ln(2/c)$ (II-65)

Um, do and dm are molecular parameters.

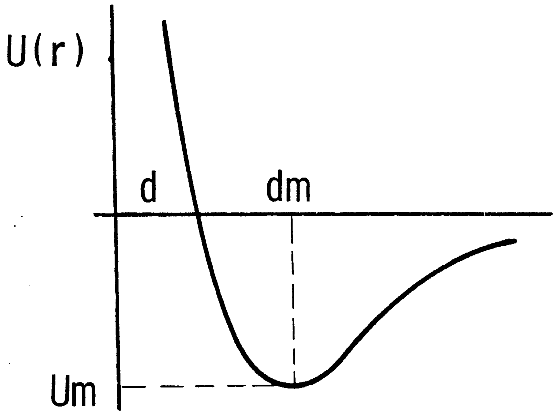

Fig. II-26. Morse Potential

The parameter c defines the curvature of the potential at dm. Small value of c gives a potential with a small curvature at dm, resulting in a wide potential well. Similarly large value of c will give a narrow potential well. Morse's potential has a finite value at the origin given by the following equation:

$$U(0) = 4Ume^{c}(d^{c}-1) \quad (II-66)$$

Second virial coefficient for this potential is obtained by inserting equation II-64 into equation II-29 and the result is as follows:

$$B(T) = 2\pi Nd^{3}F\ (c, \frac{kT}{Um}) \quad (II-67)$$

The function F is calculated by Konowlow, Taylor and Hirschfelder (82). The molecular parameters of this potential for several substances are calculated by Konowalow and Guberman (81). This potential predicts second virial data over the entire temperature range better than Lennard-Jones 12-6 potential (124).

13. Singer Potential: Singer (128) proposed a potential made up of two Gaussian functions as follows:

$$U(r) = A \exp(-ar^2) - B \exp(-br^2) \qquad \text{(II-68)}$$

where A, B, a and b are the four characteristic parameters. Neither analytical expression nor tabulated values of B are available. Singer (128) obtained these parameters for Argon only using crystal properties and showed that this potential mostly overlaps Lennard-Jones (12-6) potential.

14. Boys and Shavitt Potential: Boys and Shavitt (18) introduced a potential containing unlimited numbers of adjustable parameters. The analytical expression for the potential energy is as follows:

$$U(r) = \frac{4Um}{(r^2+B^2)^3} \sum_{i=0} C_{2i} \left[r^{2i} \exp A(1-r^2) - 1 \right] \qquad \text{(II-69)}$$

They stipulated that intermolecular separation, r, should be measured so that $U(1) = 0$ and constants A and B^2 be assigned values of 4 and 1/10. The constants C_{2i} are then adjusted to fit experimental data. For $C_o = 1$

and $C_{2i} = 0$, this potential agrees very well with Lennard-Jones (12-6) potential (18).

The second virial coefficient is given in terms of tabulated values for specific choices of constants C_o, C_2 and C_4 by Boys and Shavitt (20). Munn (106) has done further work on this potential and has recommended a simple procedure to evaluate constants C_o, C_2, C_4 and C_6. Using appropriate number of constants, shape of the potential can be changed as desired.

II. ANGLE-DEPENDENT POTENTIALS

As mentioned earlier, this discussion is divided into three subsections as angle dependency can arise due to either shape or due to polarity or due to both shape and polarity.

a) Angle-Dependency due to Shape of the Molecules

Qualitatively it is interesting to see how the second virial coefficient depends on the shape of a molecule. A simple way is to compare second virial coefficients of rigid convex bodies of several shapes. We must remember that in this case B is independent of temperature which is not in accord with the facts.

Keesom (70) carried out first such calculations for rigid ellipsoids of revolution. The results were not very encouraging and after a gap of about forty years, Isihara and Hayashida (66,67) formulated a general theory for the second virial coefficient for rigid convex molecules of any shape. This theory was extended by Kihara (74, 76, 77, 78). The second virial coefficient for these rigid molecules can be written as follows:

$$B = b_o f \tag{II-70}$$

where $$b_o = \frac{2}{3}\pi N d^3 \tag{II-71}$$

f = shape factor

The term b_o corresponds to the second virial coefficient for rigid spheres of diameter d. The shape factor f is dependent upon the curvature of the molecules and surface to volume ratio of the molecules is given by the following equation (58).

$$f = 1 + [(S_o/b_o)\ (M/4\ ) - (3/4)] \tag{II-72}$$

where $$M = \int (1/2)\ [\frac{1}{R_1} + \frac{1}{R_2}]^{ds} \tag{II-73}$$

ds = surface element for the integration

S_o = the surface area of N molecules

R_1, R_2 = principal radii of curvature of the surface at the surface element d_s.

The shape factor, f, has been evaluated for variety of nonspherical shapes (65,66,67,75,76).

1. <u>Kihara Potential</u>: Kihara (74,76,77,78) visualized the molecules having a rigid convex core, superposed with a force field outside the rigid core. In this case the energy of interaction of the two molecules is taken as a function of the shortest distance between the surfaces of the two cores. Physical significance of this concept is that the centers of forces are uniformly distributed over the core surfaces and the forces have such a fast variation with distance that major contribution to the interaction energy is due to two closest centers of forces.

The equation for the potential is as follows:

$$U = 4U_m \left[\left(\frac{d_m}{r}\right)^{12} - \left(\frac{d_m}{r}\right)^{6} \right] \qquad \text{(II-74)}$$

where r= the shortest distance between the cores

d_m = the intermolecular separation for which energy is minimum

U_m = the minimum potential energy

Second virial coefficient for this potential is given by the following equation (117, 119):

$$\frac{B}{N} = \frac{2}{3}\; d_m^3 F_3\left(\frac{U_m}{kT}\right) + M_o d_m^2 F_2\left(\frac{U_m}{kT}\right) + \left(S_o + \frac{M_o^2}{4\pi}\right) d_m F_1\left(\frac{U_m}{kT}\right)$$

$$+ V_o + \left(\frac{M_o S_o}{4\pi}\right) \qquad \text{(II-75)}$$

where the functions F_1, F_2 and F_3 are available in the form of tables (35, 36). Factors M_o, S_o and V_o arise from size and shape of the core (58).

The adjustable parameters of this model are d_m, U_m and the ones describing shape and size of the core. The usual procedure is to obtain the core shape and size parameters on the basis of molecular structure and then adjust d_m and U_m to fit experimental B(T) data. Another method is to leave size parameter adjustable, fixing only shape parameter, thereby giving us three parameters to work with. The method of evaluation of these parameters is described by Prausnitz and Keeler (118).

The core model is an extension of the shell model. This model has been fitted to heavy rare gases very well (95). Also it has been well fitted to the dipolar and quadrupolar gas data (95).

2. Corner Potential: Corner (37) approximated a long molecule by four centers of forces as shown in Fig. II-27. The potential energy for this interaction is given by the following equation:

$$U(r) = \sum_{i=1}^{4} \sum_{j=1}^{4} 4(Um)_c \left[\frac{dm_c}{r_{ij}}^{12} - \frac{dm_c}{r_{ij}}^{6}\right] \tag{II-76}$$

where r_{ij} = distance between point center i to the point center j

dm_c = minimum distance between given two centers of forces for which the potential energy is minimum

Um_c = minimum potential energy corresponding to dm_c

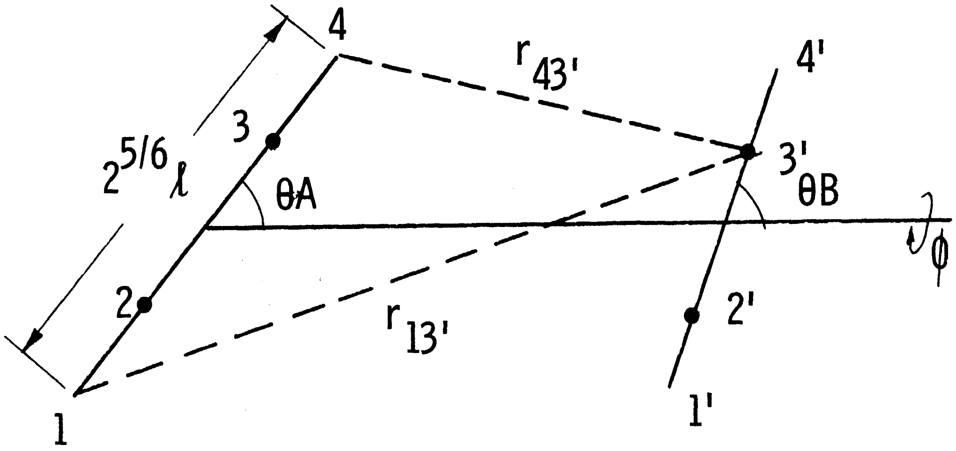

Fig. II-27. Molecular Interaction for Corner Potential

There are sixteen possible interactions in summation of Equation (II-76). Each interaction depends upon the orientation of both molecules which are given in terms of θA, θB and θ. Using Equation (II-76) in Equation (II-29) and integrating over all angles, the second virial coefficient is given by the following equation:

$$B(T) = \frac{2\ Ndm^3\alpha}{3}\ [B^*(\frac{kT}{Um}) + \beta\ \{\ 6B_1^*\ (\frac{kT}{Um}) + 4B_2^*\ (\frac{kT}{Um})\}] \qquad (II-77)$$

where $B^* = B/(2/3\pi Nd^3)$ (II-78a)

$$B^*_k = T^{*k}(d^kB^*/dT^{*k}) \qquad (II-78b)$$

$$T^* = kT/Um \qquad (II-78c)$$

$$= 1 + \frac{29}{15}\frac{1}{dm} + \frac{53}{15}\ \frac{1}{dm}\ 3 + ... \qquad (II-78d)$$

The function β in Equation (II-77) is tabulated (58). The parameters Um, and dm are sort of an average of those for all possible pairs of centers of forces. The quantity l is the characteristic length. There are three characteristic molecular parameters for this potential, namely, Um, dm and l. These molecular parameters for several substances are given in reference (58).

(b) Angle Dependency Due to Polarity of Molecules

(1) Rigid Spheres with Imbedded point dipoles: If the molecules are considered to be rigid spheres of diameter d and having centers of dipole strength μ, the potential energy is written as follows:

$$U(r,\ \theta,\ \theta_2,\ \phi_2 - \phi_1) = \infty \qquad \text{for } r < d$$

$$= -\frac{\mu^3}{r^3}\ g(\theta_1,\ \theta_2,\ \phi_2 - \phi_1) \qquad \text{for } r > d \qquad (II-79)$$

where $g(\theta_1,\ \theta_2,\ \phi_2 - \phi_1) = 2Cos\theta_1Cos\theta_2 -- Sin\theta_1Sin\theta_2Cos(\phi_2 - \phi_1)$ (II-80)

This interaction is discussed before and presented in Figure II-13. Substituting Equation (II-79) in Equation (II-29) we obtain the following expression for the second virial coefficient (70):

$$B(T) = \frac{2}{3}\pi N d^3 \left[1 - \sum_{i=1}^{\infty} \frac{G_i}{(2i)!(2i-1)} \left(\frac{\mu^2}{d^3 kT}\right)^{2i}\right] \qquad \text{(II-81a)}$$

$$= \frac{2}{3}\pi N d^3 \left[1 - \frac{1}{3}\left(\frac{\mu^2}{d^3 kT}\right)^2 - \frac{1}{75}\left(\frac{\mu^2}{d^3 kT}\right)^4 \ldots.\right] \qquad \text{(II-81b)}$$

where

$$G_i = \frac{1}{8\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi} g^{2k} \sin\theta_1 \sin\theta_2 \, d\theta_1 \, d\theta_2 \, d(\phi_2 - \phi_1) \qquad \text{(II-81c)}$$

where g is defined in Equation (II-80).

Keesom (71) extended this work to calculate the second virial coefficient for rigid spheres having point quadrupole amounts.

(2) <u>Stockmayer Potential</u>: Extending the Lennard-Jones (12-6) potential to dipole-dipole interaction, Stockmayer (132) proposed the following potential:

$$U(r_1, \theta_1, \theta_2, \phi_2 - \phi_1) = 4U_m \left[\left(\frac{d}{r}\right)^{12} - \left(\frac{d}{r}\right)^6\right] - \frac{\mu^2}{r^3} g \qquad \text{(II-82)}$$

where g is defined in Equation (IV-54) and μ is the dipole moment. Equation (II-82) was substituted in Equation (II-29) and the second virial coefficient is given as follows (59, 123):

$$B(T) = \frac{2}{3}\pi N d^3 2^{1/2} \left[\left(\frac{U_m}{kT}\right)^{1/4} \Gamma\left(\frac{3}{4}\right) - \frac{1}{4}\sum_{j=1} \frac{2^j}{j!} \sum_{i=0}^{i\leq j/2} \frac{\binom{j}{2i} \Gamma\left(\frac{2j-2i-1}{4}\right)}{(2i+1} \frac{G t^{2i}}{\left(\frac{kT}{U_m}\right)^{(j+1)/2}}\right] \qquad \text{(II-83a)}$$

where $$G = \sum_{i=0}^{p} \frac{\binom{p}{i} 3^i}{2i+1} \qquad \text{(II-83b)}$$

and $$t = 8^{-1/2} \frac{\mu^2}{U_m d^3} \qquad \text{(II-83c)}$$

In the Equation (II-83a), d is the collision diameter and t is the reduced dipole energy. The equation(II-83a) can be simply written as:

$$B = \frac{2}{3}\pi N d^3 F(\theta,t) \qquad \text{(II-84)}$$

where $F(\theta,t)$ is tabulated (123) There are two parameters, U_m and d to be determined for this potential. The method of determination of these molecular parameters along with their values for several substances are given in reference (58).

(c) Angle-Dependency Due to Shape and Polarity

Kihara Potential: O'Connell and Prausnitz (133) combined the dipole-dipole interaction with Kihara potential to obtain the following equation:

$$\begin{aligned} U(r) &= \infty && \text{for } r < d \\ &= 4U_m \left[\left(\frac{d}{r}\right)^{12} - \left(\frac{d}{r}\right)^{6} + \frac{\mu^2}{r^3} g \right] && \text{for } r > d \end{aligned} \qquad \text{(II-85)}$$

where d, U_m, and r have the same significance as that explained in Equation (II-74) and g is defined by Equation (II-80). The second virial coefficient for this potential is as follows:

$$B(T) = \frac{2}{3}\pi N d^3 F \left(\frac{kT}{U_m} \frac{\mu^2}{8^{1/2} U_m d^3}\right) \qquad \text{(II-86)}$$

The function F in Equation (II-86) is evaluated by O'Connell and Prausnitz (109) for spherical molecules only.

Suh and Storvick (134) extended this treatment to convex molecules. The expression for B(T) is:

$$B(T) = \frac{2}{3}\pi N d^3 F_c(z) + MNd^3 F_2(z) + (S+M^2/4\pi)\, NdF_1(z)$$

$$+ (V+MS/4\pi)N - \frac{2^{1/2}}{36}\pi N\, (d+d_o)^3 t^2 2H_6(y) \qquad \text{(II-87)}$$

where $z = U_m/kT$ (II-88a)

d_o = core diameter

$t = \mu^2/(8)^{1/2}\, U_m (d+d_o)^3$ (II-88b)

$y = 2\,\left(\frac{U_m}{kT}\right)^{1/2}$ (II-88c)

$H_6(y) = y^{7/2} \sum\limits_{p=0} \left[\left(\frac{yp}{p!}\, \Gamma\left(\frac{2p+1}{4}\right)\right)\right]$ (II-88d)

The functions F_i are the same as that for the Kihara potential. Quantities M, S and V are derived from shape and size of the molecule. Suh and Storvick (134)have described the method of evaluation of the molecular parameters and have calculated them for several substances. Certain unsatisfactory features in this derivation were improved by Storvick and Spurling (133) and they obtained results for the spherical molecules only.

III. COMBINATION RULES FOR INTERMOLECULAR FORCES.

The only exact rule for combination is that for the diameter of rigid sphere where interaction diameter is the arithmatic mean of the individual molecular diameters. Other rules must be regarded as empirical or semi-empirical. Therefore without explaining the theoretical connections, if any, the rules are simply listed below. For rigid spheres

$$d_{12} = \frac{1}{2}(d_{11}+d_{12}) \qquad \text{(II-89)}$$

where the subscript 1 stands for one molecular species and subscript 2 stands for the second molecular species. The subscript 12 denotes the interaction between the molecule of species one with that of species two. The parameter d will denote the characteristic intermolecular separation for the particular potential. In the following discussion, parameter U_m will denote the characteristic potential energy for that particular potential:

$$d_{12} = \frac{1}{2}(d_{11}+d_{22}) \qquad \text{(II-89)}$$

and

$$U_{m12} = \frac{(Um_{11}U_{m22})^{1/2}}{(U_{m11}+U_{m22})} \qquad \text{(II-90)}$$

Fender and Halsey (49) modified Equation (II-90) into the following expression:

$$U_{m12} = \frac{2U_{m11}U_{m22}}{(U_{m11}+U_{m22})} \qquad \text{(II-91)}$$

Another rule for d_{12} is (95)

$$d_{12} = (d_{11}d_{22})^{1/2} \tag{II-92}$$

Mason (94) proposed the following combination rules for the Exp-6 potential:

$$\alpha_{12} = \frac{1}{2}(\alpha_{11}+\alpha_{22}) \tag{II-93}$$

$$d_{m12} = \frac{1}{2}(d_{m11}+d_{m22}) \tag{II-94}$$

and

$$U_{m12} = (U_{m11}U_{m22})^{1/2} \tag{II-90}$$

Nain and Saxena (108) proposed the following combination rules for the Buckingham-Carrà-Konowalow potential:

$$\frac{\alpha_{12+6}}{\underset{e}{\alpha_{12}}} = \left(\frac{\alpha_{11+6}}{\underset{e}{\alpha_{11}}}\right)\left(\frac{\alpha_{22+6}}{\underset{e}{\alpha_{22}}}\right)^{1/2}$$

$$d_{m12} = 2\,\alpha_{12}/\left(\frac{\alpha_{11}}{d_{m11}} + \frac{\alpha_{22}}{dm_{22}}\right)$$

$$U_{m12} = (U_{m11}U_{m22})^{1/2}\,\frac{\alpha_{12}}{(\alpha_{11}\alpha_{22})^{1/2}}\left[\frac{d_{m11}d_{m22}}{d_{m\,12}^{\;2}}\right]^2\left(\frac{\alpha_{11}+\alpha_{22}}{\underset{e}{2\alpha_{12}}}\right) \tag{II-97}$$

For the Morse potential combination, rules were proposed by Saxena and Gambhir (124) as follows:

$$U_{m12} = (U_{m11}U_{m22})^{1/2} \qquad \text{(II-90)}$$

$$d_{m12} = (\frac{C_{11}}{d_{011}} d_{m11} + \frac{C_{22}}{d_{022}} d_{m22})/(\frac{C_{11}}{d_{011}} + \frac{C_{22}}{d_{022}}) \qquad \text{(II-98)}$$

$$d_{012} = d_{m12} - 2\ln 2/(\frac{C_{11}}{d_{011}} + \frac{C_{22}}{d_{022}}) \qquad \text{(II-99)}$$

$$C_{12} = \frac{1}{2}(\frac{C_{11}}{d_{011}} d_{m11} + \frac{C_{22}}{d_{022}} d_{m22}) - \ln 2 \qquad \text{(II-100)}$$

For the Stockmayer potential, combination rules for unlike polar molecules were given by Rowlinson (122) and they are as follows:

$$d_{12} = (d_{11} + d_{22})/2 \qquad \text{(II-89)}$$

$$U_{m12} = (U_{m11}U_{m22})^{1/2} \qquad \text{(II-90)}$$

$$t_{12} = \frac{\mu_{11}\mu_{22}}{8^{1/2} U_{m12} d_{12}^{3}} \qquad \text{(II-101)}$$

For the interaction between a polar and a nonpolar molecule, combinatory rules for the molecular parameters of Stockmayer's potential are given by the following equations (122):

$$d_{np} = \frac{1}{2}(d_n + d_p)\,\alpha^{-1/6} \qquad \text{(II-102)}$$

$$(U_m)_{n,p} = (U_{mp}U_{mn})^{1/2}\,\alpha^{2} \qquad \text{(II-103)}$$

where $$\alpha = 1 + \frac{1}{4}\,\frac{\alpha_n \mu^2}{4\,U_m d_p 3 d_n 3}\,(\frac{U_{mp}}{U_{mn}})^{1/2} \qquad \text{(II-104)}$$

n,p = subscripts to denote nonpolar and polar molecule
α_n = polarizability of the non-polar molecule
d_p, d_n = collision diameters of polar and nonpolar molecular species.

For the Kihara potential, combinatory rules for the two parameters, d and U_m are the same as given in Equations (II-89) and (II-90), but the interaction virial coefficient, B_{12}, has a modified form in terms of individual shape and size factors (58) which is as follows:

$$2B_{AB} = \frac{4\pi}{3} d^3 F_3 \left(\frac{U_{m12}}{kT}\right) + (M_{11}+M_{22}) d_{12}{}^2 F_2 \left(\frac{U_{m12}}{kT}\right)$$
$$+ \left(S_{11}+S_{22}+M_{11}M_{22}/2\pi\right) d_{12} F_1 \left(\frac{U_{m12}}{kT}\right)$$
$$+ \left(V_{11}+V_{22} + \frac{M_{22}S_{11}+M_{11}S_{22}}{4\pi}\right) \qquad \text{(II-105)}$$

This concludes the basic review of literature on intermolecular potentials. For further reading, the work of Klein (79) on Lennard-Jones, Kihara, Exp-6 and Square Well potential is recommended.

IV. DIPOLE MOMENTS OF R-22 AND R-115

Smyth and McAlpine (129) reported the dipole moment of chlorodifluoromethane, R-22, to be 1.39 debye. Later on Fuoss (51) estimated that dipole moment of R-115 is 0.14 debye. Lately Giacomo and Smyth (52) reported a value for the dipole moment of R-115 to be 0.52 debye.

CHAPTER III

EXPERIMENTAL WORK

E.I. du Pont de Nemours and Company supplied twenty-two pounds of R-502, whose gas chromatographic analysis showed that it contained organic impurities less than 0.02 wt% and moisture 7 ppm by weight. The vapor phase contained 0.33 vol. % of air. The chromatographic analysis was carried out by the Du Pont Company.

Experimental work to determine physical properties of R-502 was carried out in several phases. Vora (138) used static method to measure vapor pressure up to about 16 psia (-100 to -40 F). Hossain (61) using sealed tubes containing calibrated floats measured saturated liquid density from -165 to 180 F as well as critical temperature. PVT behavior was determined using a bellows PVT cell in the ranges of 0-2000 psia and 80 to 250 F.

Equipment systems and operating procedures are described below and details are given in the Appendices.

A. PVT BEHAVIOR OF R-502

A.1 Bellows PVT Cell

Bellows PVT cell was designed by Bhada (15). Cell and auxiliary equipment are given schematically in Fig. III-1. The whole experimental set-up can be divided into the following sections:

1. Bellows PVT cell.
2. Pressure measurement system.
3. Temperature control system.
4. Temperature measurement system.

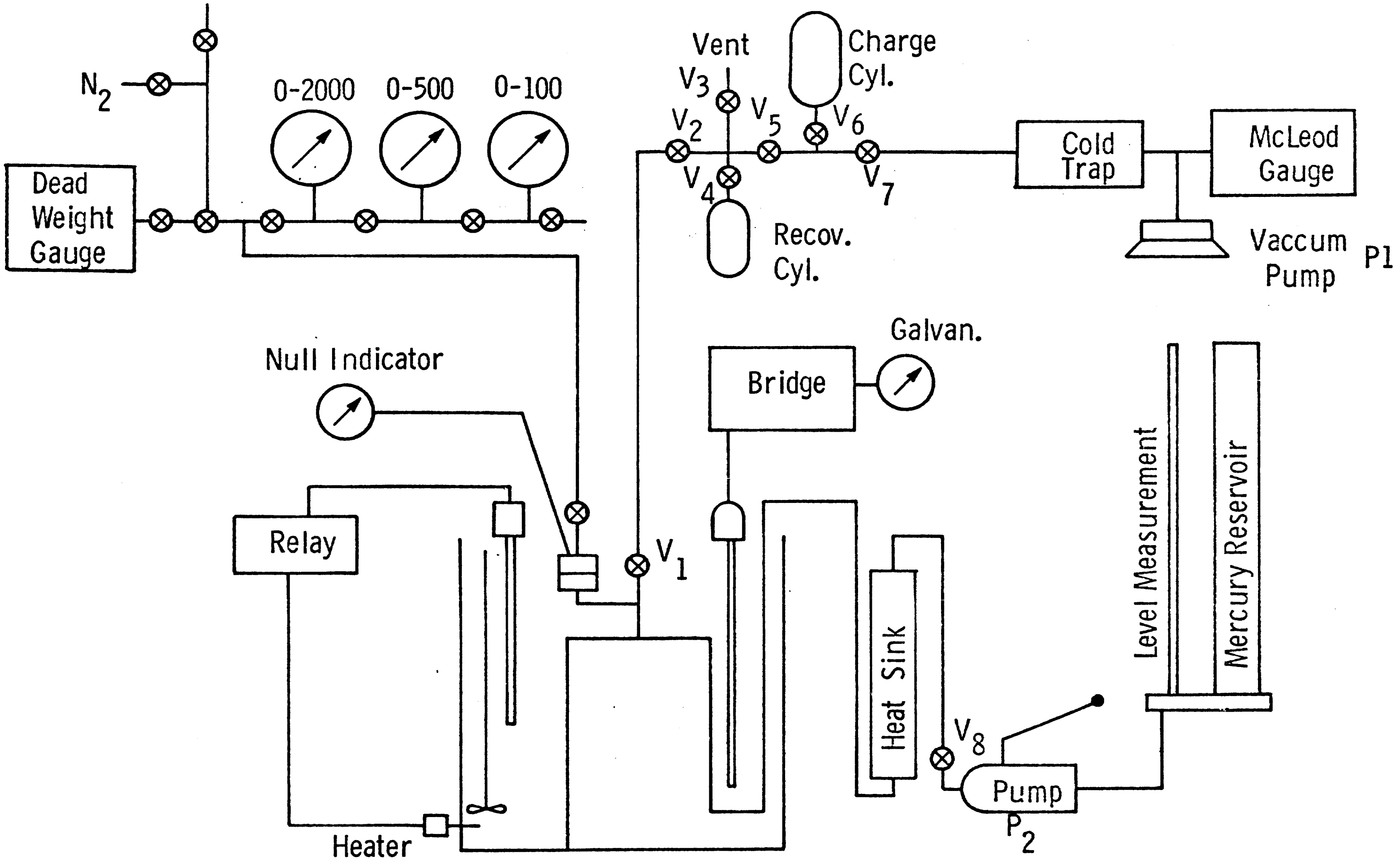

Figure. III. 1 System for PVT Measurements Using Bellows PVT Cell

5. Charging and recovery system.

Details of the PVT cell are given in Fig. III-2. It consists of a bellows enclosed in a thick-walled cylindrical shell, all made of stainless steel 316. The bellows is suspended from the top and is provided with an inlet to admit the test sample. Space between bellows and the cylindrical shell is filled with a hydraulic fluid (mercury in present case). Appropriate ports are provided for bleeding and draining of the hydraulic fluid in the space between the bellows and the cylindrical shell. A hand operated hydraulic pump is used for forcing hydraulic fluid from the reservoir. Volume of the bellows is determined in terms of the level of the mercury in the reservoir which is measured on a glass gauge.

The pressure measurement system consists of a PACE-diaphragm pressure transducer, null indicator, pressure gauges, dead weight tester and a supply of high pressure nitrogen gas. The pressure transducer, located in the bath in which PVT cell was submerged, received system pressure on one side of the diaphragm. Nitrogen pressure was applied to the other side of the diaphragm to balance the system pressure, so that differential pressure should not exceed 50 psi in normal operations. Balance of the pressure was indicated by a null indicator. The pressure transducer worked on the principle of magnetic reluctance. Nitrogen pressure was measured on an appropriate gauge. Three gauges of ranges 0-100, 0-500 and 0-2000 psi were accurated calibrated *in situ* by a dead weight tester before and after experimental runs.

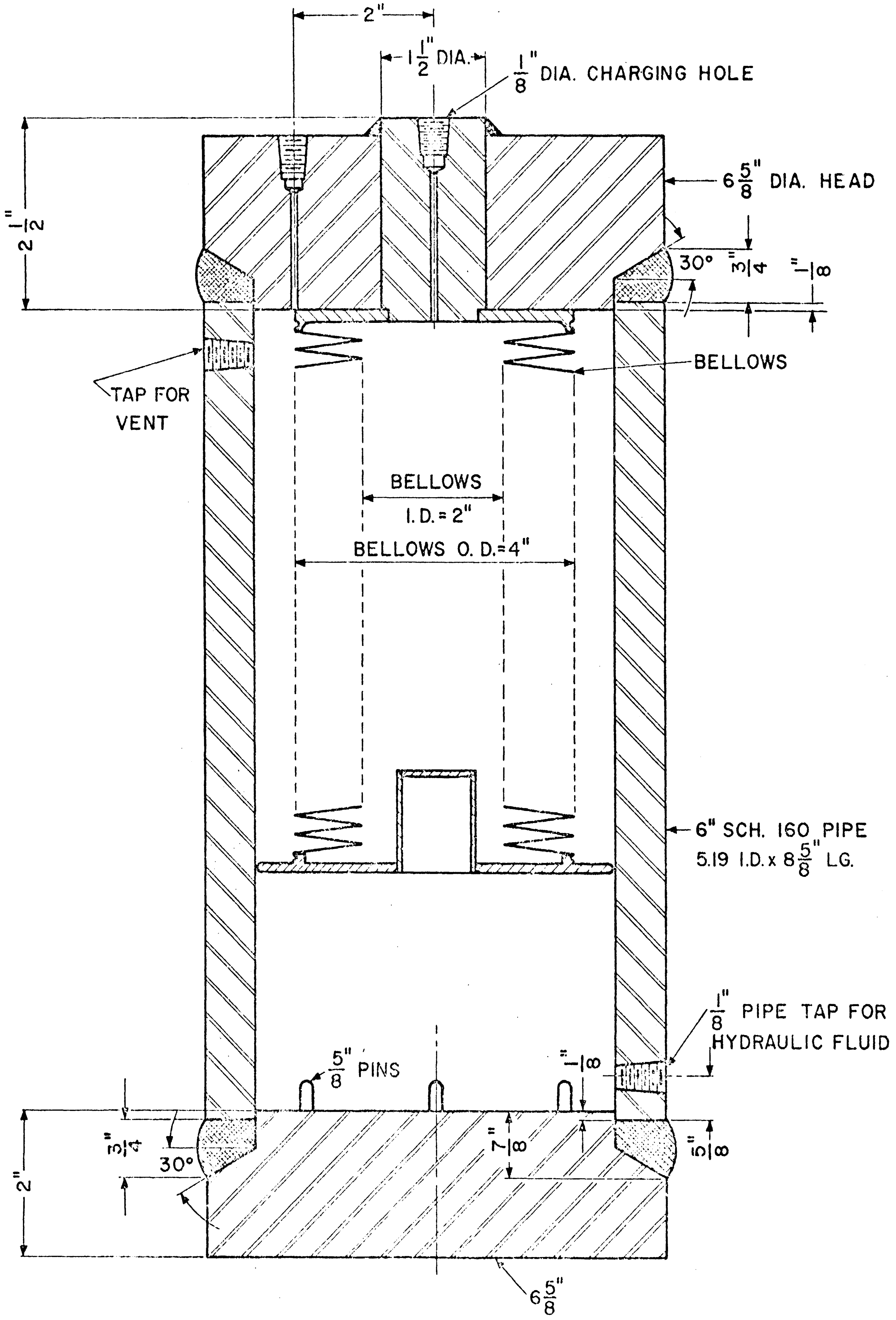

Fig. III.2 Details of the Bellows PVT Cell (15)

The temperature control system, consisting of a thermoregulator. relay and heater, gives an on-off type control of the temperature of the bath fluid in which PVT cell and the pressure transducer are immersed. A magnetically adjustable mercury contact thermoregulator, immersed partially in the bath fluid sends signals to the relay whether temperature of the bath fluid exceeds from that adjusted on the thermoregulator. Accordingly, the heater is switched off or turned on. At all temperatures of measurements above room temperature, cooling is due to heat lost to ambient and at room temperature measurements a cooling coil with tap water running through it, is used. The bath is well stirred.

Bath temperature is measured by a platinum resistance thermometer. It was calibrated by the National Bureau of Standards. Resistance of the thermometer is measured by a wheatstone bridge connected to a galvanometer.

The charging and recovery system consists of a vacuum pump, McLeod gauge, charging cylinder and a recovery cylinder. The vacuum pump is capable of pulling a vacuum as low as one micron. Weights of the cylinders are determined by a very accurate balance whose weights were calibrated.

A-1.b Procedure of Operation

The experimental procedure is divided into the following three sections.

1. Charging the PVT cell
2. Data observation
3. Recovery of the test sample from the PVT cell

Notations used in the following description are explained in Fig. III-1.

Initially the bellows are compressed to their minimum volume, allowing air to escape through the vent valve V_3. Then valve V_3 is closed and the PVT cell is evacuated by means of the vacuum pump P_1 to a vacuum of less than ten microns. The bath is kept at room temperature. In another operation, the charging cylinder is filled with liquid R-502 from the inverted supply cylinder. The charging cylinder is held inverted during the charging operation so that only liquid, having the given composition, is charged without getting any small impurities of vapor phase into the system. During charging operation valves V_3, V_4 and V_7 are kept closed. The PVT cell and the lines are under vacuum at this stage. Then valve V_6 is opened slowly and pressure is allowed to build in the PVT cell. Some pressure buildup can be absorbed by expanding the bellows to a desired volume. The pressure is continuously monitored through the pressure transducer. Nitrogen pressure must be manipulated to balance the pressure transducer diaphragm at all times. After the pressure reaches vapor pressure at the bath temperature, liquid mixture will trickle into the PVT cell. About fifteen minutes are given for the liquid to fill the PVT cell and then valves V_1 and V_6 are closed. Now valve V_4 on the evacuated recovery cylinder is opened allowing liquid in the lines to flash into the cylinder. The recovery cylinder is held at -190 C by liquid nitrogen. At such low temperature, the mixture being solid, all liquid in the lines go into the recovery cylinder and freezes. To assure that all the residual amount of test sample in the lines is recovered, all the lines from the PVT cell to valve V_7 are heated by an electric tape to about

200 F for about 20 minutes. The recovery cylinder is detached, and allowed to warm up to room temperature. From the weights before and after of the charging cylinder as well as recovery cylinder, mass of the charge can be determined.

Now the temperature of the bath is controlled at the desired temperature by means of a Doty magnetic thermoregulator connected to a relay circuit which powers the heaters in the bath. The temperature fluctuation was of the order of ±0.04 F over one full run. In observing the data we started with the largest volume depending on the pressure reading. The PVT cell is calibrated in terms of the level of mercury in the mercury reservoir. Then the cell is compressed by means of the hydraulic pump P_2 to a desired volume. About half an hour is allowed for the test sample to reach thermal equilibrium with the bath and then pressure is recorded. This procedure is repeated as desired. Finally bellows is decompressed to bring the volume to the same as one start s out and again pressure is recorded. This provides a check to see whether the test sample has leaked. The same procedure of data observation is repeated with different amount of charges and different temperatures.

In the recovery operation, all lines are evacuated to a vacuum of less than 10 microns. The preweighed evacuated recovery cylinder is positioned in its place. With the PVT cell at a temperature, usually higher than room temperature, valve V_4 is opened. The recovery cylinder is held at -190 C using liquid nitrogen. The lines are heated and kept at a temperature less than the bath temperature so that no condensation of vapor can take place in the lines. The bellows is slowly compressed to its smallest volume and then about 45 minutes time is allowed for all test sample to transfer to the recovery cylinder. Valve V_4 is then closed. The recovery cylinder is allowed to warm up to room temperature and is weighed. From the weights of the charging cylinder before and after charging, the mass of the test sample is calculated which can be compared with the value obtained before in the charging procedure. Both values should agree within the precision of weighing, otherwise the data is discarded.

A-1c. Experimental Precision

Temperature were measured to ±0.001 F using a platinum resistance thermometer. The on-off temperature contral gave a sinusoidal variation in the bath temperature (Appendix A). By recording the average resistance, estimated precision in the temperature value was ±0.04 F at the worst.

Pressure measurements were believed to be accurate to ±0.17%. Volume calibrations were estimated to be accurate to ±0.45% at the lowest bellows volume and ±0.20% at the highest bellows volume. The accuracy of the whole weighing procedure was estimated to be ±0.05%. The specific volumes obtained were estimated to be accurate to ±0.5% at the lowest bellows volume and ±0.25% at the highest bellows volume.

B. VAPOR PRESSURE OF R-502

Vapor pressure of R-502 was measured in two parts:

1) low-pressure experiment, and 2) high pressure experiment. Vora (138) measured low vapor pressure by the static method. For high vapor pressure measurements the PVT cell was used. Equipment and procedures of operation are discussed in general here and details are given in Appendix B.

B-1. Low Vapor Pressure Measurements:

B-1a. Experimental System:

Experimental system is similar to that used by Hou (62) and is presented schematically in Fig. III-3. It can be divided into the following sections:

1) The isoteniscope
2) Pressure measurement system
3) Temperature control system
4) Temperature measurement system
5) Charging system

The isoteniscope is a glass tube of adequate capacity to hold a liquid sample. The isoteniscope is immersed in a constant temperature bath.

The pressure measurement system consists of a mechanical vacuum pump, mercury diffusion pump, mercury U tube manometer and a cathetometer. One leg of the mercury U tube manometer is continuously exposed to a vacuum of about one micron created by a combination of mercury diffusion pump with the mechanical vacuum pump. The other leg of the mercury leg

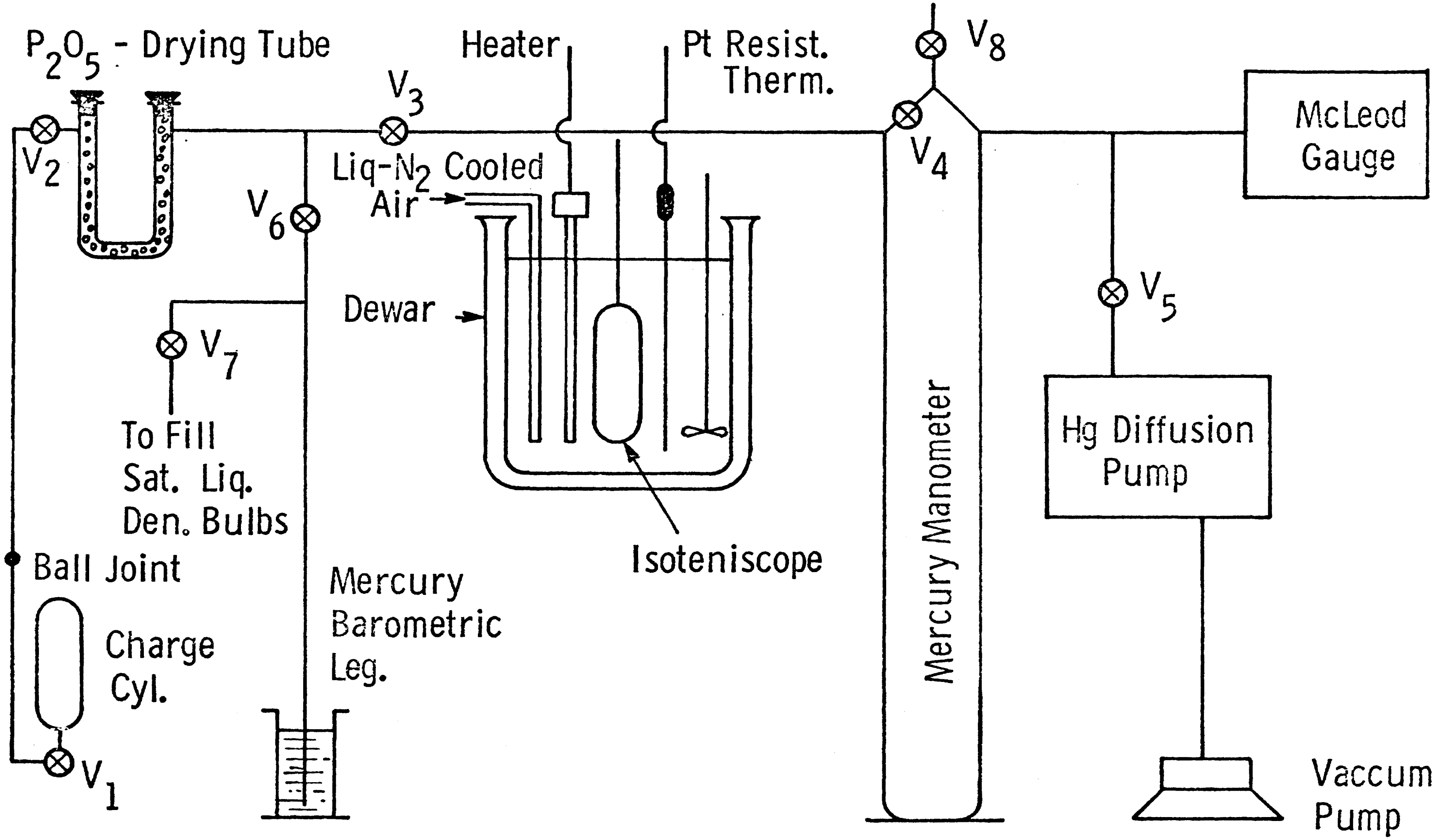

Fig. III.3 System for Low Vapor Pressure Measurements is subjected to the vapor pressure of the liquid. The difference in the level of mercury in the two legs is measured by a cathetometer giving directly the vapor pressure of the liquid sample at the bath temperature.

Temperature control system consists of a heater, supply of compressed air and a dewar filled with liquid nitrogen. Compressed air is cooled by the liquid nitrogen and is bubbled through the bath fluid. A constant rate of bubbling is adjusted. Also the heater is adjusted for constant heat input. When the rate of cooling is equal to the rate of heating, the bath attains a constant temperature. This constant temperature is measured by a platinum resistance thermometer as explained before. The bath fluid is well mixed by an air driven stirrer. Normal propanol was used as the bath fluid.

The charging system consists of a charging cylinder, a drying tube and vacuum pumps. The drying tube is filled with P_2O_5 and the vacuum pumps are the same as those used for the pressure measurements.

B-1b. Procedure of Operation:

Operating procedure can be divided into two parts as follows:

1) Charging procedure
2) Observation of the data

In terms of notation used in Fig. III-3, the procedure of operation can be explained as follows. With all valves except V_1, V_7, and V_8 open, evacuation of the system is carried out to one micron vacuum. Then valve V_4 is closed and V_1 opened very minutely. Simultaneously the isoteniscope is cooled rapidly to -190 C by liquid nitrogen so that the test sample is collected in it. After assuring that an adequate amount of R-502 is condensed in the isoteniscope, valves V_1 and V_3 are closed off.

Now equipment is ready for the observations. Temperature of the bath is controlled at desired values by trial and error. Pressure is recorded from the manometer readings and corresponding temperature is measured by the resistance of the platinum resistance thermometer. Values of pressure were obtained at different temperatures. In one run the full range of 16 psia can be covered. The amount of test sample is normally vented to the atmosphere through valve V_8 after the experiment.

B-1c. Experimental Precision:

Temperature can be measured to the accuracy of ±0.001 F by the platinum resistance thermometer. The temperature control was precise to ±0.1 F. This amounts to a maximum error in the vapor pressure values of ±0.03 psi.

The cathetometer can read level differences of the magnitude of 0.001 cm. Precision in reading mercury levels was expected to be ±0.1 mm giving differences in the levels accurate to ±0.2 mm corresponding to a pressure of ±0.005 psi.

The total estimated precision in the vapor pressure values is ±0.035 psi and the temperature values, ±0.1 F.

B.2 High Vapor Pressure Measurements

An azeotropic mixture exerts constant pressure at a constant temperature in the two phase region. R-502 was compressed in the two phase region from dew point to bubble point with about 3 or 4 pressure data points at a temperature. The average of the data points was regarded as the vapor pressure of R-502 at the temperature. Details and precision of temperature and pressure measurements are the same as that given for PVT measurements.

C. SATURATED LIQUID DENSITY OF R-502

Hossain determined saturated liquid density of R-502 by the method used by Hou (62). The experimental system is presented schematically in Fig. III-4, and can be divided as:

1) Saturated liquid density bulb
2) Temperature control system
3) Temperature measurement system

Saturated liquid bulb contains a liquid, whose density has to be determined, and a calibrated density float. The temperature at which density of the liquid equals density of the float is determined.

The temperature control system is the same as that used for vapor pressure measurements for temperature below room temperature. For temperatures above room temperature, carefully controlled heat input through a knife heater was used. Temperature was continuously monitored by the platinum resistance thermometer which was shielded.

According to the principle of Archimedes, the apparent weight of the float when totally submerged in the liquid is zero if the liquid has the same density as the float; consequently, the float has no tendency to either rise to the surface of the liquid or sink to the bottom. Experimentally, this point is difficult to detect, if not impossible. Temperature of the bath is allowed to rise very slowly and movement of the float is noticed. Initially density of the float being lower than that of the liquid, it floats on the top. The temperature at which the float starts sinking to the bottom is roughly noticed. Then the bath is allowed to cool and the heating rate is very carefully adjusted to determine precise temperature at which the float starts

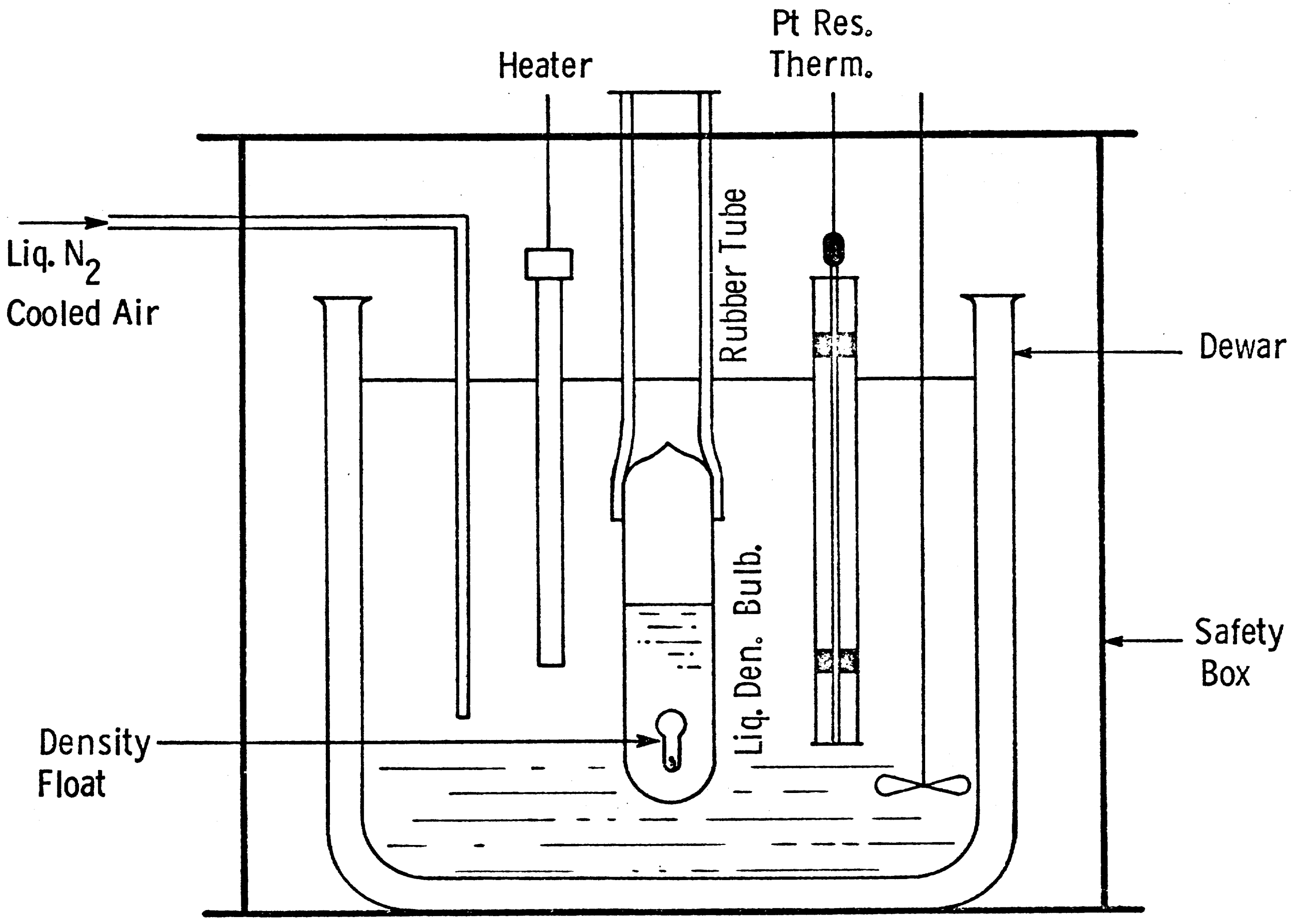

Fig. III.4 System for Saturated Liquid Density Measurements sinking. Now the heating rate is reduced and the exact temperature at which the float starts rising is noted. The two temperatures should not differ more than 0.05 F.

Temperature values are estimated to be precise to ±0.05 F which amounts to an error of about ±0.02% in density values. Possible errors in volumes of floats amount to about ±0.01%. Float densities are expected to be precise to ±0.06%. Total estimated precision in density values is ±0.1% with temperature values accurate to ±0.05 F.

D. CRITICAL TEMPERATURE OF R-502

Critical temperature of R-502 was determined by the constant volume method. A saturated liquid density bulb containing a float whose density is close to the critical density was used in observing the disappearance and reappearance of the meniscus between the vapor and liquid phase. Experimental system is the same as that used in determining saturated liquid densities of R-502. An ethylene glycol bath equipped with an electric heater is used to control temperature of R-502 in the bulb. After making sure that the bulb is not likely to crack, a shielded platinum resistance thermometer is used to measure temperature. The average of temperatures of meniscus disappearance and reappearance is taken as the critical temperature of R-502. The critical temperature is estimated to be precise within ±0.03 F.

CHAPTER IV

EXPERIMENTAL RESULTS

All experimental data of R-502 is given in Appendix E. In this chapter the data is analyzed graphically as well as algebraically. Details of algebraic correlations are given in Appendices F, G and H.

Vapor Pressure of R-502: The vapor pressure data covering the range of -150 to +180 F corresponding to the pressure range of 0.4 to 590 psia is presented as a semilog plot of P vs. 1/T in Fig. IV-1. This data was correlated by Martin and Downing (90) using the following equation:

$$\ln P = A + \frac{B}{T} + C\ln T + DT + \frac{E(F-T)}{FT} \ln(F-T) \qquad \text{(IV-1)}$$

where

P = psia

T = F + 459.67

A = 24.51091456

B = -8453.14404297

C = -0.36983496

D = 0.0040211239

E = 533.7385

F = 654.0

Equation (IV-1) is compared with the experimental data and other vapor pressure values in Tables IV-3 through IV-7. These comparisons are summarized in the following table.

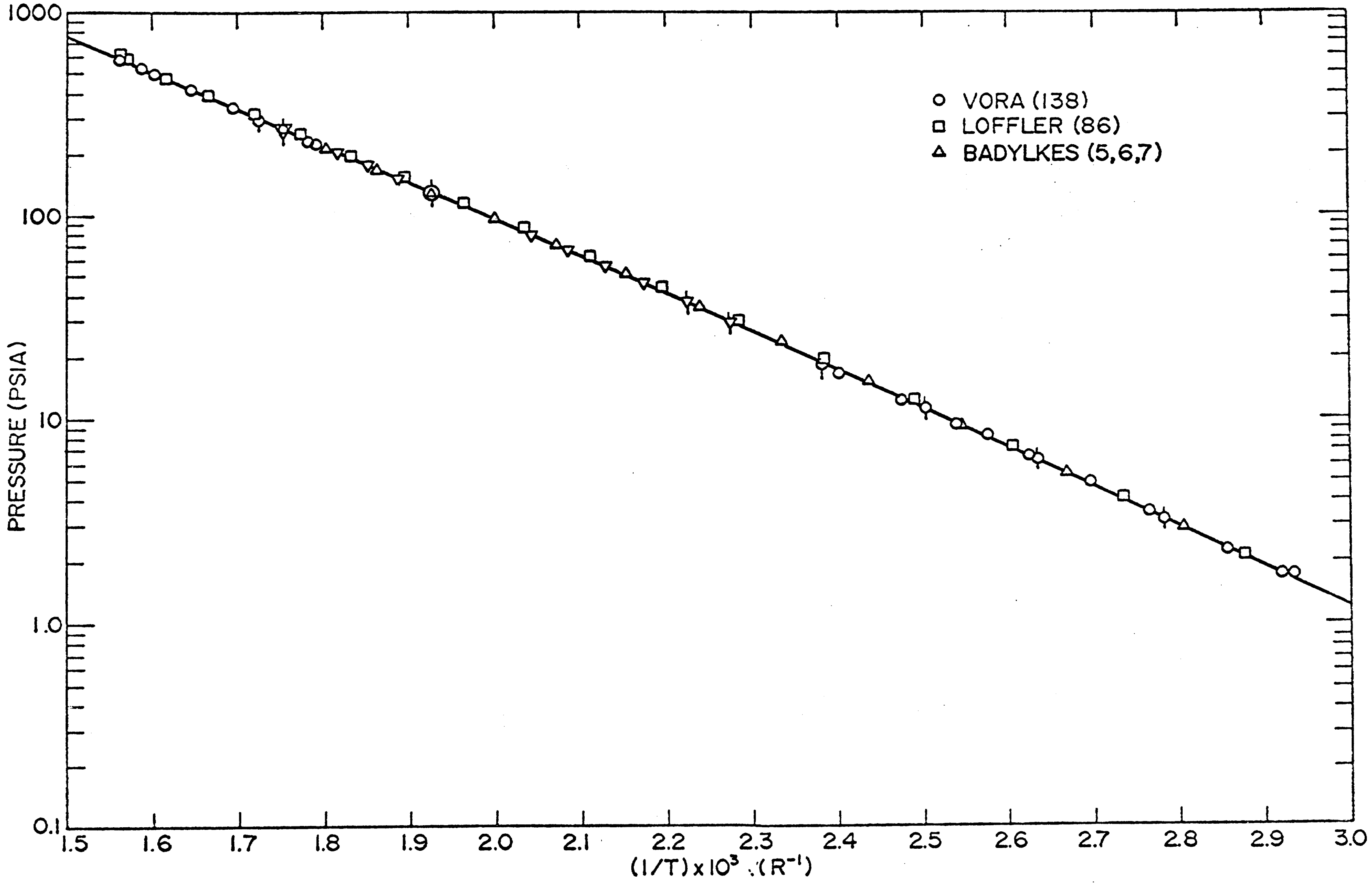

Fig. IV.1 Vapor Pressure of R-502.

TABLE IV-1

Summary of Comparison of Equation (IV-1) With Vapor Pressure Data

Source	Average	Average Absolute % Dev.
This Work	-0.22	1.28
Badylkes (5,6,7)	+0.35	0.35
Loeffler (86)	+3.55	3.55
Downing (42)	-0.12	0.57
Du Pont (47)	-0.24	0.69

Examination of Tables IV-3 through IV-7 points out that Equation (IV-1) predicts well the experimental data of this work and that of Downing (42). The vapor pressure values of Badylkes (5,6,7) and Du Pont (47) being based on the experimental data of Downing (42) consequently are predicted by Equation (IV-1) very well. Loffler's values (86) seem to lie unusually lower to the values of this investigation and the discrepancy cannot be analyzed since details of his work are not available.

Saturated Liquid Density of R-502

The experimental saturated liquid density measurements covering the temperature range of -165 to 179 F are presented in Fig. IV-2. This figure also includes saturated vapor densities (90) and the rectilinear diameter for R-502 as well as R-22 and R-115. The data points are fitted to the following equation by Martin and Downing (90). Details of the algebraic correlation are given in Appendix H.

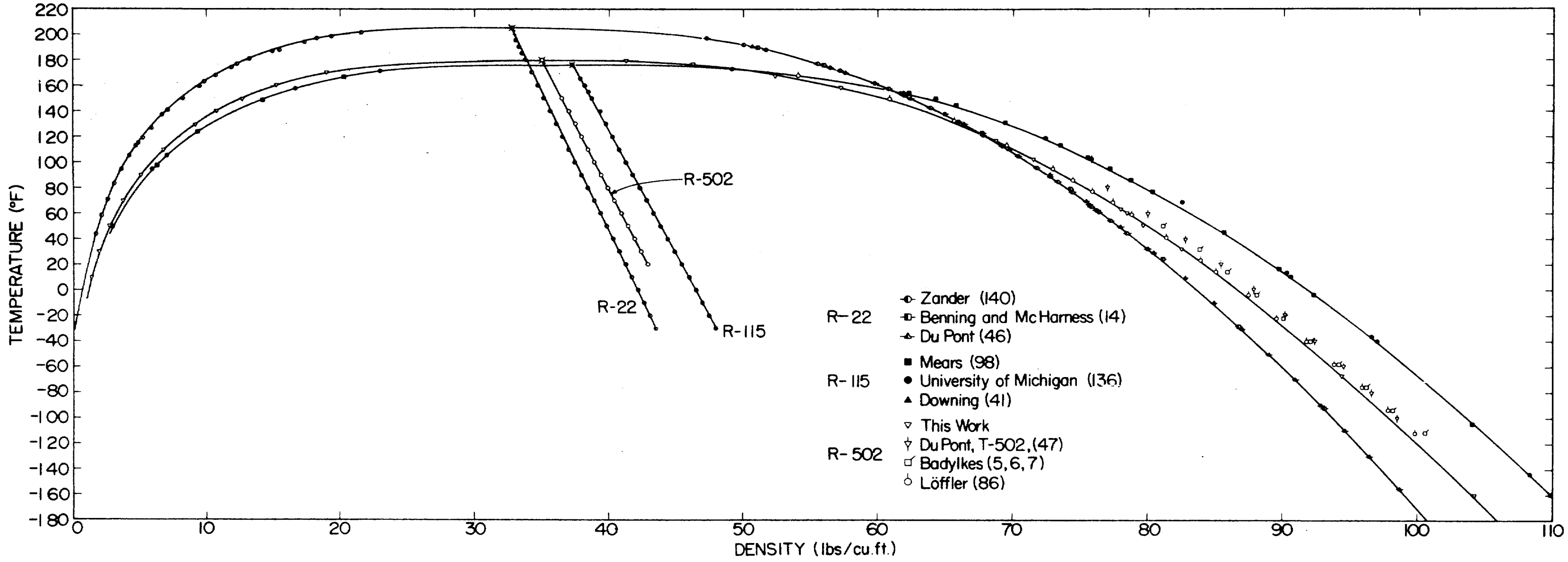

Fig. IV-2. Saturated liquid and vapor density plot for R-22, R-115 and R-502.

$$d_{SL} = A + B(1-T_R)^{1/3} + C(1-T_R)^{2/3} + D(1-T_R) + E(1-T_R)^{4/3} \qquad \text{(IV-2)}$$

where d_{SL} = density of saturated liquid

$T_T = T/T_c = (F+459.67)/639.56$

$A = 35.0$

$B = 53.48437$

$C = 63.86417$

$D = -70.08066$

$E = 48.47901$

Equation (IV-2) is compared with the experimental data of this investigation and the saturated liquid density values reported by others in Table IV-8 through Table IV-11. These comparisons are summarized in Table IV-2.

TABLE IV-2

Summary of Comparison of Equation (IV-2) and Saturated Liquid Density Values

Source	Average % Dev.	Average Absolute % Dev.
Hossain (61)	+0.075	0.11
Badylkes (5,6,7)	+1.20	1.20
Loffler (86)	+0.47	0.47
Du Pont (47)	+1.96	1.96

Examination of Tables IV-8 through IV-11 points out that values of this work agree very well with the saturated liquid density values reported by Loffler (86) over almost the entire range except near the critical point. Comparison of Equation (IV-2) with the works of Badylkes (5,6,7) and Du Pont (47) is relatively poor. The discrepancy between the values of this investigation and Du Pont (47) cannot be analyzed since details of the work are not available.

Critical Constants: The average of a number of observations of the temperature at which the meniscus of liquid R-502 in an appropriate liquid density bulk disappeared and reappeared gave the critical temperature as 179.89 F or T_c = 639.56 R. Substituting this value in Equation (IV-1), Martin and Downing (90) calculated the critical pressure as 591 psia. Martin and Downing (90) reported a critical density of 35.0 lbs/cu.ft. This was confirmed by plotting a rectilinear diameter of the saturated liquid and vapor density values for R-502 (Fig. IV-2).

Rectilinear Diameter: A plot of saturated liquid and vapor density values for R-502 gives the rectilinear diameter (Fig. IV-2). Vapor density values given by Martin and Downing (90) were used. Rectilinear Diameter for R-502 can be described by the following equation:

$$\frac{d_{sl} + d_{SV}}{2} = A(1-T_R) + d_c \qquad \text{(IV-3)}$$

where

d_{sl} = saturated liquid density

d_{SV} = saturated vapor density

d_c = critical density = 35.0 lbs/cu.ft.

$T_R = T/T_c = (F+459.67)/639.56$

$A = 31.544$

Eqn. (IV-3) is compared with the rectilinear diameter points in Table IV-12.

PVT Behavior of R-502: PVT behavior of R-502 was determined over the temperature range of 80 to 250 F, up to 2000 psia and up to two times the critical density. It is presented as a PV plot in Fig. IV-3. The experimental data is converted into compressibility fact Z and is presented as a function of reduced pressure in Fig. IV-4. The compressibility factor is defined as:

$$Z = \frac{P\underline{V}}{RT} \tag{IV-4}$$

where

P = pressure

$\underline{V}$ = specific volume

T = absolute temperature

R = gas constant

Molecular weight of R-502 was taken as 111.641. No disagreements were found between the compressibility factors of this investigation and the generalized compressibility factors prepared from PVT investigations of several refrigerants.

PVT data is correlated with the following equation:

$$P_R = \frac{T_R}{Z_c(V_R-b/V_c)} + \frac{A_2 + B_2T_R + C_2e^{-kT}}{Z_c^{\,2}(V_R-b/V_c)} + \frac{A_3 + B_3T_R + C_3e^{-kT}}{Z_c^{\,3}(V_R-b/V_c)^3}$$

$$+ \frac{A_4 + B_4T_R + C_4e^{-kT_R}}{Z_c^{\,4}(V_R-b/V_c)^4} + \frac{A_5 + B_5T_R}{e^{a_1V_R}(1+c_1e^{a_1V_R})} + \frac{A_6 + B_6T_R}{e^{a_2V_R}(1+c_2e^{a_2V_R})} \tag{IV-5}$$

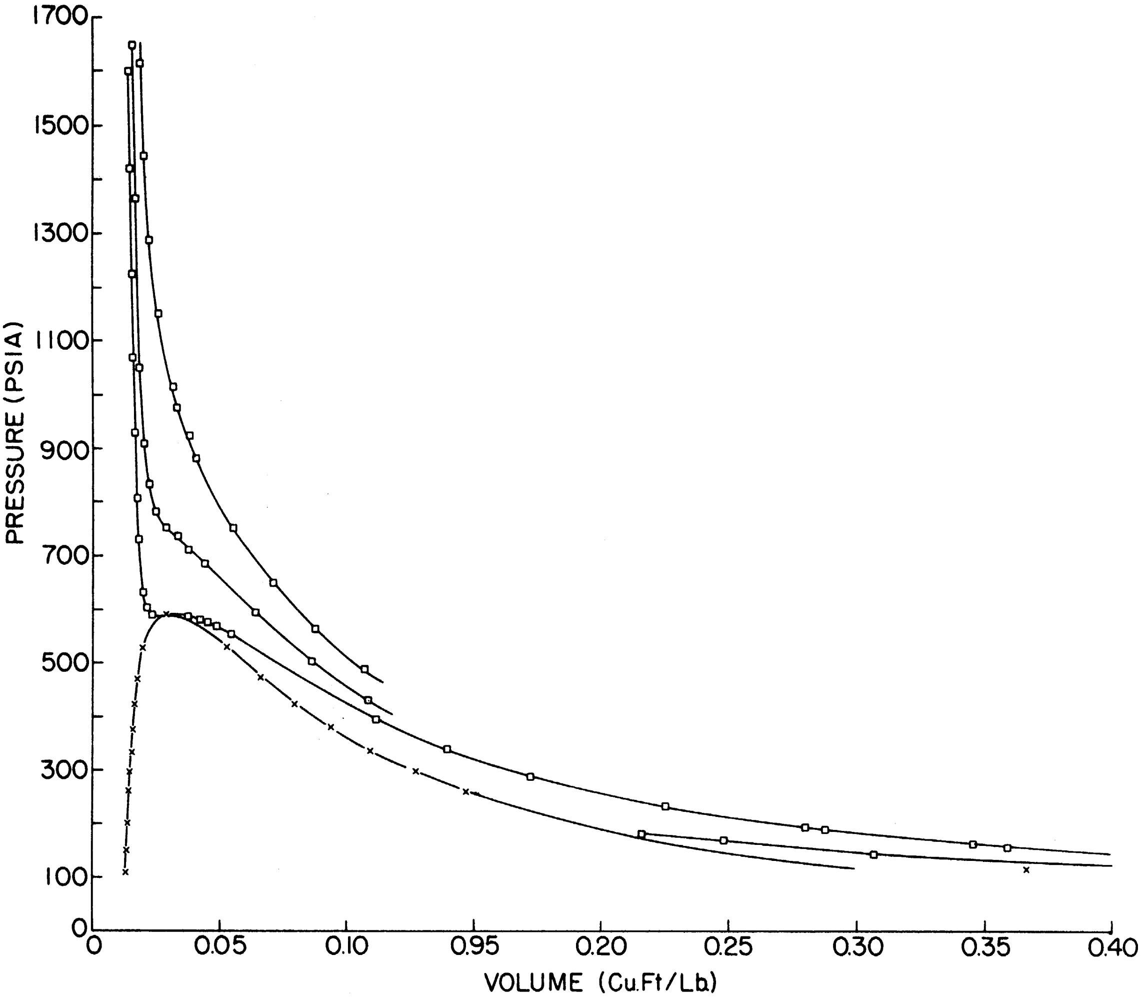

Fig. IV-3. PVT behavior of R-502

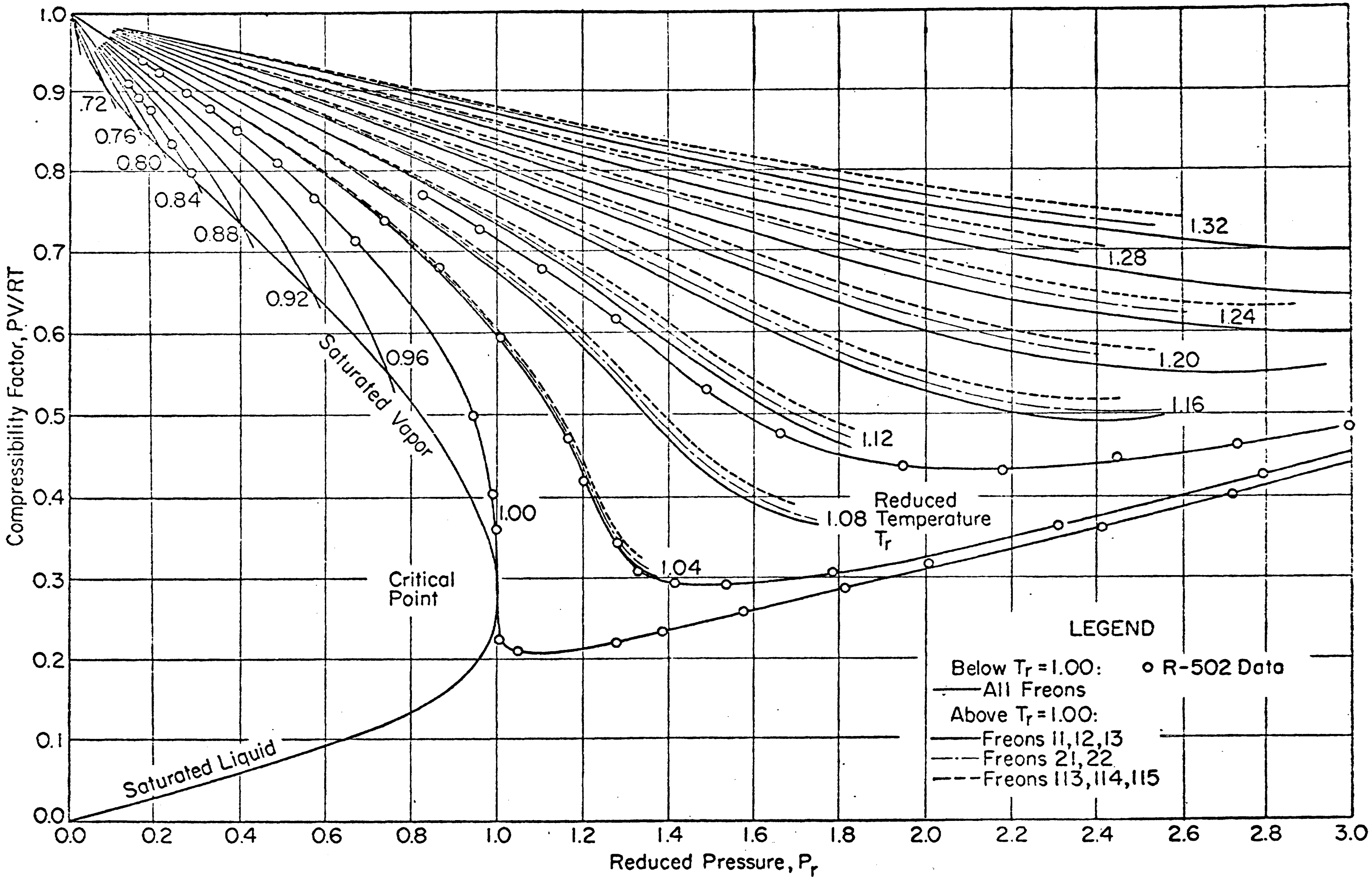

Fig. IV.4 Compressibility Factor of R-502.

where $P_R = P/P_c = (\text{psia})/591.0$

$V_R = V/V_c = (\text{lbs/cu.ft.})/0.028571$

$T_R = T/T_c = (F+459.57)/639.56$

$Z_c = P_c V_c/RT_c = (591.0)(0.028571)/(0.0961248)(639.56)$

$= 0.27466$

$a_1 = 16.00$

$a_2 = 22.00$

$b = 0.118328$

$C_1 = 3.5\text{x}10^{-6}$

$A_2 = -0.409519$

$B_2 = 0.146538$

$C_2 = 0.224995\text{x}10^{1}$

$A_3 = 0.211483\text{x}10^{-2}$

$B_3 = 0.198065\text{x}10^{-1}$

$C_3 = 0.815044$

$A_4 = 0.132335\text{x}10^{-2}$

$B_4 = 0.197201\text{x}10^{-2}$

$C_4 = 0.654305\text{x}10^{-1}$

$A_5 = 0.793470\text{x}10^{5}$

$B_5 = 0.957628\text{x}10^{5}$

$A_6 = 0.256235\text{x}10^{7}$

$B_6 = 0.248641\text{x}10^{7}$

Equation (IV-5) is compared with the experimental data in Table IV-13.

The experimental data was taken at approximately four reduced temperatures namely $T_R = 0.8$, 1.0, 1.04 and 1.1. At reduced temperature 0.8 we are dealing with low pressures and the isotherm is fairly short since it is limited by the two phase region. At the critical temperature, the isotherm goes through inflection at the critical point. The difficult shape of the isotherm is more apparent in the compressibility chart where $T_R = 1$ curve starts out with $Z = 1$ and curves steeply down to Z_c and then immediately goes up as P_R increases. Similar behavior is observed with the isotherm of 1.04 T_R because it is still close to the critical temperature and exhibits a deep well. As we go to higher temperatures, say 1.1 T_R, the bowl in the isotherm curve becomes shallow.

Therefore, merit of an equation of state may be quickly judged by observing how it fairs at these four isotherms. From Table IV-13 it is apparent that appreciable deviations are observed at low temperature, but they are still within the total experimental precision. At the critical temperature, fit is very good all the way up to two times the critical density. The deviations reported in Table IV-13 are pressure deviations rather than volume deviations. Pressure deviations are a very severe test of the test data particularly in the high pressure, high density regions. The fit is again good around T_R = 1.04 where data goes up to 1.9 times the critical density. Equation (IV-5) compares with the data very well at T_R = 1.1 up to 1.6 times the critical density. Thus in overall, Equation (IV-5) predicts the PVT behavior of R-502 well and within the precision of experimental measurements (Appendices A and B).

TABLE IV-3

IV-3. Comparison of Equation IV-1 and Experimental Vapor Pressure Data for R-502 Obtained in This Work

t F	P psia	P_{eq} psia	Percent Deviation
-151.12	0.400	0.404	-1.11
-129.88	1.097	1.048	4.50
-118.68	1.712	1.645	3.90
-117.14	1.719	1.746	-1.55
-109.65	2.296	2.313	-0.72
-109.60	2.307	2.317	-0.42
-109.51	2.329	2.325	0.19
-109.19	2.445	2.352	3.80
-108.83	2.398	2.383	0.63
-103.45	2.958	2.891	2.26
-98.03	3.481	3.490	-0.25
-97.37	3.523	3.569	-1.32
-88.89	4.851	4.729	2.51
-88.49	4.911	4.790	2.46
-78.45	6.452	6.562	-1.70
-76.95	6.890	6.867	0.33
-71.57	8.322	8.057	3.18
-67.71	8.916	9.010	-1.05
-65.82	9.338	9.508	-1.82
-56.96	11.860	12.146	-2.41
-55.19	12.304	12.737	-3.52
-54.85	12.901	12.853	0.37
-49.71	14.265	14.713	-3.14
-43.02	16.725	17.445	-4.31
98.46	224.380	226.271	-0.84
98.48	226.530	226.331	0.09
98.58	225.350	226.629	-0.57
100.52	232.050	232.471	-0.18

TABLE IV-3 (contd.)

t F	P psia	P_{eq} psia	Percent Deviation
100.54	233.060	232.532	0.23
102.71	240.780	239.196	0.66
110.85	266.630	265.447	0.44
120.98	302.770	301.000	0.58
130.04	335.080	335.703	-0.19
130.05	336.620	335.743	0.26
130.33	339.630	336.862	0.82
139.51	379.100	375.161	1.04
147.26	414.900	410.097	1.16
149.22	424.200	419.338	1.15
150.38	433.100	424.888	1.90
150.42	430.300	425.081	1.21
152.41	436.860	434.749	0.48
152.50	435.550	435.191	0.08
163.27	497.110	490.963	1.24
164.66	499.940	498.616	0.26
169.55	527.450	526.472	0.19
179.65	588.800	589.399	-0.10
179.74	589.340	589.999	-0.11
179.75	589.340	590.066	-0.12

TABLE IV-4

IV-4. Comparison of Equation IV-1 and Vapor Pressure Values for R-502 reported by Badylkes (5,6,7)

t F	P psia	P_{eq} psia	Percent Deviation
-112.00	2.121	2.120	0.02
-103.00	2.942	2.937	0.16
-94.00	4.014	3.998	0.39
-85.00	5.382	5.355	0.50
-76.00	7.106	7.066	0.56
-67.00	9.250	9.194	0.60
-58.00	11.880	11.809	0.60
-49.00	15.070	14.986	0.56
-40.00	18.900	18.802	0.52
-31.00	23.450	23.344	0.45
-22.00	28.810	28.698	0.39
-13.00	35.070	34.954	0.33
-4.00	42.320	42.207	0.27
5.00	50.660	50.553	0.21
14.00	60.180	60.089	0.15
23.00	70.990	70.913	0.11
32.00	83.190	83.126	0.08
41.00	96.880	96.828	0.05
50.00	112.190	112.121	0.06
59.00	129.210	129.108	0.08
68.00	148.100	147.893	0.14
77.00	168.900	168.583	0.19
86.00	191.800	191.289	0.27
95.00	217.000	216.128	0.40
104.00	244.500	243.225	0.52

TABLE IV-5

IV-5. Comparison of Equation IV-1 and Vapor Pressure Values for R-502 Reported by Loeffler (86)

t F	P psia	P_{eq} psia	Percent Deviation
-112.00	2.146	2.120	1.19
-103.00	3.000	2.937	2.09
-94.00	4.100	3.998	2.48
-85.00	5.526	5.355	3.09
-76.00	7.320	7.066	3.47
-67.00	9.550	9.194	3.72
-58.00	12.290	11.809	3.91
-49.00	15.580	14.986	3.82
-40.00	19.550	18.802	3.82
-31.00	24.400	23.344	4.33
-22.00	29.980	28.698	4.28
-13.00	36.450	34.954	4.10
-4.00	43.940	42.207	3.94
5.00	52.610	50.553	3.91
14.00	62.460	60.089	3.80
23.00	73.770	70.913	3.87
32.00	86.410	83.126	3.80
41.00	100.500	96.828	3.65
50.00	116.200	112.121	3.51
59.00	133.700	129.108	3.43
68.00	153.100	147.893	3.40
77.00	174.600	168.583	3.45
86.00	198.000	191.289	3.39
95.00	223.700	216.128	3.38
104.00	251.900	243.225	3.44
113.00	282.500	272.719	3.46
122.00	315.800	304.766	3.49
131.00	352.100	339.550	3.56

TABLE IV-5 (contd.)

t °F	P psia	P_{eq} psia	Percent Deviation
140.00	391.700	377.297	3.68
149.00	434.400	418.292	3.71
158.00	480.900	462.925	3.74
167.00	531.100	511.759	3.64
176.00	585.800	565.710	3.43
180.90	617.300	597.801	3.16

TABLE IV-6

IV-6. Comparison of Equation IV-1 and Vapor Pressure Values for R-502 Reported by Downing (42).

t F	P psia	P_{eq} psia	Percent Deviation
-20.00	29.800	30.007	-0.69
-10.00	37.600	37.257	0.91
-10.00	36.900	37.257	-0.97
0.0	46.000	45.776	0.49
10.00	56.000	55.697	0.54
20.00	67.500	67.156	0.51
30.00	80.100	80.287	-0.23
40.00	95.200	95.229	-0.03
40.00	95.700	95.229	0.49
50.00	111.600	112.121	-0.47
60.00	130.800	131.105	-0.23
70.00	150.700	152.322	-1.08
80.00	176.100	175.922	0.10
90.00	201.100	202.058	-0.48
100.00	230.800	230.895	-0.04
110.00	260.500	262.612	-0.81
110.00	265.000	262.612	0.90
130.00	332.700	335.544	-0.85
150.00	419.700	423.063	-0.80

TABLE IV-7

IV-7. Comparison of Equation IV-1 and Vapor Pressure Values for R-502 Reported by Du Pont (47)

t F	P psia	P_{eq} psia	Percent Deviation
-100.00	3.230	3.261	-0.97
-80.00	6.280	6.258	0.35
-60.00	11.280	11.182	0.87
-40.00	18.970	18.802	0.88
-20.00	30.220	30.007	0.71
0.0	45.940	45.776	0.36
20.00	67.140	67.156	-0.02
40.00	94.900	95.229	-0.35
60.00	130.300	131.105	-0.62
80.00	174.600	175.922	-0.76
100.00	229.100	230.895	-0.78
120.00	295.000	297.415	-0.82
140.00	373.800	377.297	-0.94
160.00	467.300	473.389	-1.30

TABLE IV-8

IV-8. Comparison of Equation IV-2 and Experimental Saturated Liquid Density Data for R-502 Obtained in This Work

t F	d lbs/cu.ft.	d_{eq} lbs/cu.ft.	Percent Deviation
-161.80	104.220	104.023	0.19
-67.32	94.410	94.410	0.00
32.00	82.560	82.564	-0.00
50.55	79.680	79.979	-0.38
60.25	78.500	78.555	-0.07
63.79	78.020	78.020	0.00
64.83	77.940	77.861	0.10
102.01	71.580	71.592	-0.02
116.25	68.760	68.760	0.00
157.86	57.290	57.293	-0.00
168.78	52.240	52.136	0.20
176.22	46.270	46.270	0.00
179.08	41.250	41.452	-0.49

TABLE IV-9

IV-9. Comparison of Equation IV-2 and Saturated Liquid Density Values for R-502 Reported by Badylkes (5,6,7)

t F	d lbs/cu.ft.	d_{eq} lbs/cu.ft.	Percent Deviation
-112.00	100.530	99.087	1.44
-103.00	99.090	98.166	0.93
-94.00	98.160	97.236	0.94
-85.00	97.240	96.294	0.97
-76.00	96.190	95.341	0.88
-67.00	95.160	94.375	0.82
-58.00	94.160	93.396	0.81
-49.00	93.170	92.403	0.82
-40.00	92.080	91.394	0.75
-31.00	91.130	90.367	0.84
-22.00	90.080	89.323	0.84
-13.00	89.050	88.258	0.89
-4.00	88.050	87.172	1.00
5.00	86.950	86.062	1.02
14.00	85.870	84.926	1.10
23.00	84.820	83.761	1.25
32.00	83.680	82.564	1.33
41.00	82.470	81.331	1.38
50.00	81.180	80.059	1.38
59.00	80.030	78.741	1.61
68.00	78.620	77.373	1.59
77.00	77.360	75.947	1.83
86.00	75.850	74.453	1.84
95.00	74.320	72.881	1.94
104.00	72.510	71.215	1.79

TABLE IV-10

IV-10. Comparison of Equation IV-2 and Saturated Liquid Density Values for R-502 Reported by Loeffler (86)

t F	d lbs/cu.ft.	d_{eq} lbs/cu.ft.	Percent Deviation
-112.00	99.720	99.087	0.64
-103.00	98.780	98.165	0.62
-94.00	97.850	97.236	0.63
-85.00	96.790	96.294	0.51
-76.00	95.890	95.341	0.57
-67.00	94.870	94.375	0.52
-58.00	93.880	93.396	0.52
-49.00	92.760	92.403	0.39
-40.00	91.800	91.394	0.44
-31.00	90.740	90.367	0.41
-22.00	89.570	89.323	0.28
-13.00	88.550	88.258	0.33
-4.00	87.430	87.172	0.29
5.00	86.230	86.062	0.19
14.00	85.050	84.926	0.15
23.00	83.910	83.761	0.18
32.00	82.680	82.564	0.14
41.00	81.390	81.331	0.07
50.00	80.140	80.059	0.10
59.00	78.920	78.741	0.10
68.00	77.450	77.373	0.10
77.00	75.950	75.947	0.00
86.00	74.500	74.453	0.06
95.00	72.930	72.881	0.07
104.00	71.260	71.215	0.06
113.00	69.520	69.435	0.12
122.00	67.630	67.516	0.17
131.00	65.640	65.418	0.34

TABLE IV-10 (contd.)

t F	d lbs/cu.ft.	d_{eq} lbs/cu.ft.	Percent Deviation
140.00	63.380	63.083	0.47
149.00	60.850	60.416	0.71
158.00	57.860	57.238	1.08
167.00	54.100	53.138	1.78
176.00	48.210	46.518	3.51

TABLE IV-11

IV-11. Comparison of Equation IV-2 and Saturated Liquid Density Values for R-502 Reported by Du Pont (47)

t F	d lbs/cu.ft.	d_{eq} lbs/cu.ft.	Percent Deviation
-100.00	98.490	97.857	0.64
-80.00	96.550	95.766	0.81
-60.00	94.520	93.615	0.96
-40.00	92.400	91.394	1.09
-20.00	90.180	89.088	1.21
0.0	87.840	86.682	1.32
20.00	85.390	84.152	1.45
40.00	82.800	81.470	1.61
60.00	80.040	78.592	1.81
80.00	77.070	75.457	2.09
100.00	73.800	71.968	2.48
120.00	70.080	67.956	3.03
140.00	65.590	63.083	3.82
160.00	59.490	56.430	5.14

TABLE IV-12

IV-12. Comparison of Equation IV-3 and Rectilinear Diameter Values for R-502

t F	d lbs/cu.ft.	d_{eq} lbs/cu.ft.	Percent Deviation
479.67	42.886	42.886	0.0
489.67	42.393	42.393	0.00
499.67	41.898	41.900	-0.00
509.67	41.389	41.406	-0.04
519.67	40.880	40.913	-0.08
529.67	40.368	40.420	-0.13
539.67	39.875	39.927	-0.13
549.67	39.375	39.433	-0.15
559.67	38.878	38.940	-0.16
569.67	38.403	38.447	-0.11
579.67	37.934	37.954	-0.05
589.67	37.473	37.461	0.03
599.67	36.992	36.967	0.07
609.67	36.478	36.474	0.01
619.67	35.970	35.981	-0.03
629.67	35.440	35.488	-0.13

TABLE IV-13

IV-13. Comparison of Equation IV-5 and PVT Data of R-502

$\underline{V}$ cuft/lb	T=(F+459.67) R	P_{exp} psia	V/0.028571	T/639.56)	P_{exp}/591.0	P_{calc}/591.0	%Dev.
0.582420	541.140	81.950	20.385006	0.846	0.139	0.138	0.82
0.466240	541.130	99.620	16.318645	0.846	0.169	0.168	0.52
0.404380	541.140	116.940	14.153512	0.846	0.198	0.190	4.11
0.307140	541.140	141.290	10.750061	0.846	0.239	0.239	0.16
0.248410	541.140	166.230	8.694480	0.846	0.281	0.282	-0.22
0.216550	541.130	178.800	7.579364	0.846	0.303	0.312	-3.10
0.577660	639.490	100.030	20.218403	1.000	0.169	0.169	0.05
0.461020	639.490	123.530	16.135942	1.000	0.209	0.209	0.19
0.358770	639.640	154.190	12.557138	1.000	0.261	0.262	-0.48
0.345300	639.500	160.530	12.085681	1.000	0.272	0.271	0.15
0.287570	639.620	188.540	10.065101	1.000	0.319	0.319	0.06
0.279680	639.500	193.430	9.788947	1.000	0.327	0.327	0.23
0.225160	639.530	232.430	7.880718	1.000	0.393	0.393	0.13
0.172130	639.610	288.490	6.024640	1.000	0.488	0.488	0.01
0.139340	639.610	338.240	4.876973	1.000	0.572	0.572	0.00
0.111480	639.630	393.490	3.901859	1.000	0.666	0.668	-0.26
0.054600	639.590	555.360	1.911029	1.000	0.940	0.941	-0.18
0.049090	639.600	569.260	1.718176	1.000	0.963	0.966	-0.26
0.045340	639.600	576.260	1.586924	1.000	0.975	0.979	-0.44
0.042200	639.600	581.760	1.477022	1.000	0.984	0.988	-0.41
0.037760	639.620	586.260	1.321620	1.000	0.992	0.997	-0.50
0.037560	639.580	586.770	1.314620	1.000	0.993	0.997	-0.41
0.023180	639.570	590.280	0.811312	1.000	0.999	1.006	-0.68
0.022820	639.540	594.270	0.798712	1.000	1.006	1.007	-0.18
0.021370	639.600	603.260	0.747961	1.000	1.021	1.029	-0.78
0.020370	639.560	624.270	0.712961	1.000	1.056	1.061	-0.40
0.019880	639.570	634.260	0.695810	1.000	1.073	1.086	-1.20
0.018300	639.600	729.610	0.640510	1.000	1.235	1.246	-0.90

TABLE IV-13 (contd.)

0.017680	639.530	806.470	0.618809	1.000	1.365	1.362	0.16
0.016980	639.560	930.270	0.594309	1.000	1.574	1.566	0.53
0.016430	639.550	1068.270	0.575059	1.000	1.808	1.799	0.49
0.015960	639.560	1224.270	0.558608	1.000	2.072	2.070	0.07
0.015510	639.540	1418.290	0.542858	1.000	2.400	2.410	-0.44
0.015180	639.570	1602.290	0.531308	1.000	2.711	2.725	-0.52
0.014830	639.580	1837.790	0.519058	1.000	3.110	3.130	-0.67
0.014660	639.580	1975.290	0.513108	1.000	3.342	3.358	-0.48
0.037610	664.060	707.740	1.316370	1.038	1.198	1.199	-0.09
0.028910	664.040	751.740	1.011865	1.038	1.272	1.281	-0.71
0.025060	664.050	782.540	0.877113	1.038	1.324	1.339	-1.12
0.022280	664.040	834.040	0.779812	1.038	1.411	1.416	-0.35
0.020380	664.030	909.740	0.713311	1.038	1.539	1.543	-0.26
0.018730	664.030	1051.640	0.655560	1.038	1.779	1.788	-0.50
0.017050	664.040	1366.820	0.596759	1.038	2.313	2.326	-0.56
0.016240	664.060	1650.220	0.568409	1.038	2.792	2.776	0.58
0.015630	664.050	1962.320	0.547058	1.038	3.320	3.241	2.39
0.108940	666.150	433.400	3.812957	1.042	0.733	0.734	-0.03
0.086400	666.130	503.160	3.024045	1.042	0.851	0.853	-0.17
0.063970	666.140	593.460	2.238984	1.042	1.004	1.005	-0.04
0.043500	666.150	689.260	1.522523	1.042	1.166	1.167	-0.04
0.033780	666.140	736.960	1.182318	1.042	1.247	1.250	-0.27
0.107400	708.990	488.710	3.759056	1.109	0.827	0.831	-0.47
0.087960	708.960	563.510	3.078646	1.109	0.953	0.959	-0.60
0.071050	708.970	649.010	2.486787	1.109	1.098	1.105	-0.62
0.055680	708.960	752.010	1.948829	1.109	1.272	1.277	-0.36
0.040880	709.040	882.510	1.430821	1.109	1.493	1.501	-0.50
0.033170	708.950	977.000	1.160967	1.108	1.653	1.666	-0.79
0.038760	712.500	924.600	1.356620	1.114	1.564	1.568	-0.21
0.032100	712.540	1016.600	1.123517	1.114	1.720	1.731	-0.62

TABLE IV-13 (contd.)

0.026050	712.560	1151.600	0.911764	1.114	1.949	1.961	-0.66
0.022850	712.570	1289.300	0.799762	1.114	2.182	2.172	0.44
0.020830	712.580	1445.900	0.729061	1.114	2.447	2.432	0.60
0.019480	712.570	1613.300	0.681810	1.114	2.730	2.747	-0.64
0.018680	712.590	1759.000	0.653810	1.114	2.976	3.025	-1.65
0.017870	712.610	1956.200	0.625459	1.114	3.310	3.401	-2.75

CHAPTER V

PREDICTION OF THE PROPERTIES OF R-502

One of the objectives of this work is to devise methods to predict the properties of R-502 from those of its components. Since this is just one mixture, the methods we use will need more testing before they can be regarded as rules. The following discussion is divided into PVT behavior, vapor pressure, saturated liquid density, critical constants and intermolecular potentials.

PVT Behavior

The experimental determinations of PVT behavior for R-22 have been made by Michels (99) and Zander (140). The data is presented as a P-T plot in Fig. V-1. Their values are in mutual agreement as can be seen from a few isochores which are close to each other. The PVT data is correlated with the following equation:

$$P_R = \frac{T_R}{Z_c(V_R-b/V_c} + \frac{A_2+B_2T_R+C_2e^{-kT_R}}{Z_c{}^2(V_R-b/V_c)^2} + \frac{A_3+B_3T_R+C_3e^{-kT_R}}{Z_c{}^3(V_R-b/V_c{}^3)}$$

$$+ \frac{A_4+B_4T_R+C_4e^{-kT_R}}{Z_c{}^4(V_R-b/V_c)^4} + \frac{A_5+B_5T_R}{e^{a_1V}(1+c_1e^{a_1V})} + \frac{A_6+B_6T_R}{e^{a_2V}(1+c_2e^{a_2V})} \qquad \text{(V-1)}$$

where the constants are given in Table V-1. Input conditions required to solve the constants in Eqn. (V-1) are given in Table V-2. Eqn. (V-1) is compared with the experimental data in Tables V-14 through V-16. The correlation covered the entire range of Michel's data with the following deviations in pressure values.

TABLE V-1

Values of Constants in Eqn. (V-1) for R-22, R-115 and R-502

Constant	R-22	R-115	R-502*	R-502**
P_c(psia)	721.906	456.0	593.79	591.0
T_c(R)	664.5	635.56	638.23	639.56
V_c(ft^3/lb)	0.030525	0.02681	0.028622	0.028571
R	0.124098	0.069468	0.0961248	0.0961248
Z_c	0.2672	0.2769	0.2770	0.2747
a_1	16.00	16.00	16.00	16.00
a_2	22.00	22.00	22.00	22.00
b/V_c	0.108523	0.12640	0.122732	0.118328
c_1x10^6	3.5	3.5	3.5	3.5
c_2x10^6	1.4	1.4	1.4	1.4
A_2	-0.417902	-0.405920	-0.400673	-0.409519
B_2	0.153671	0.142469	0.141223	0.146538
C_2	-2.22487	-2.24052	-2.32088	-2.24995
A_3	0.191762x10^{-1}	-0.426782x10^{-2}	-0.752109x10^{-2}	0.211483x10^{-2}

TABLE V-1 (contd.)

Constant	R-22	R-115	R-502*	R-502**
B_3	0.370338×10^{-2}	0.265288×10^{-1}	0.280848×10^{-1}	0.198065×10^{-1}
C_3	0.795797	0.808223	0.842313	0.815044
A_4	-0.146404×10^{-2}	0.235928×10^{-2}	0.299498×10^{-2}	0.132335×10^{-2}
B_4	0.710054×10^{-3}	-0.305903×10^{-2}	$-0.0353417 \times 10^{-2}$	-0.197201×10^{-2}
C_4	-0.633150×10^{-1}	-0.644044×10^{-1}	-0.676293×10^{-1}	-0.654305×10^{-1}
A_5	-0.357334×10^{4}	-0.121940×10^{6}	-0.156243×10^{6}	-0.79347×10^{5}
B_5	0.199891×10^{5}	0.138356×10^{6}	0.172659×10^{6}	0.957628×10^{5}
A_6	0.103874×10^{7}	0.367427×10^{7}	0.445685×10^{7}	0.256235×10^{7}
B_6	-0.962803×10^{7}	-0.359833×10^{7}	-0.438091×10^{7}	-0.248641×10^{7}
k	3.0	3.0	3.0	3.0

---

* Values for mixing rules

**Values for best PVT correlation

TABLE V-2

Input Conditions to Solve Constants in Eqn. V-1
for R-22, R-115 and R-502

Factor	R-22	R-115	R-502*	R-502**
$f_2(T_c)$	-0.375	-0.375	-0.375	-0.375
$f_3(T_c)$	0.0625	0.0625	0.0625	0.0625
$f_4(T_c)$	-0.003906	-0.003906	-0.003906	-0.003906
$\ln f_5(T_c)$	9.706	9.706	9.706	9.706
$\ln f_6(T_c)$	11.2377	11.2377	11.2377	11.2377
a_1	16.00	16.00	16.00	16.00
a_2	22.00	22.00	22.00	22.00
$c_1 x10^6$	3.5	3.5	3.5	3.5
$c_2 x10^6$	1.4	1.4	1.4	1.4
b/V_c	0.108523	0.1264	0.122732	0.118328
k	3.0	3.0	3.0	3.0
$(dP_R/dT_R)^+_{1.5V_c}$	3.91	3.95	3.93	3.92
$(dP_R/dT_R)_{\rho_c}$	7.40	7.55	7.45	7.45
$(dP_R/dT_R)^+_{1.4\rho_c}$	14.10	14.40	14.20	14.10
$(dP_R/dT_R)_{1.8\rho_c}$	23.80	23.80	23.80	23.80
$(d^2P_R/dT_R^2)_{\rho_c}$	0.0	0.0	0.0	0.0
$(d^2P_R/dT_R^2)_{1.8\rho_c}$	0.0	0.0	0.0	0.0
$(BP_c/RT)_{1.8T_c}$	-0.740	-0.730	-0.736	-0.735
T_B/T_C	2.3	2.3	2.3	2.3

+The slopes are evaluated as T goes to infinity
*Values given by the method of prediction
**Values obtained for best data correlation

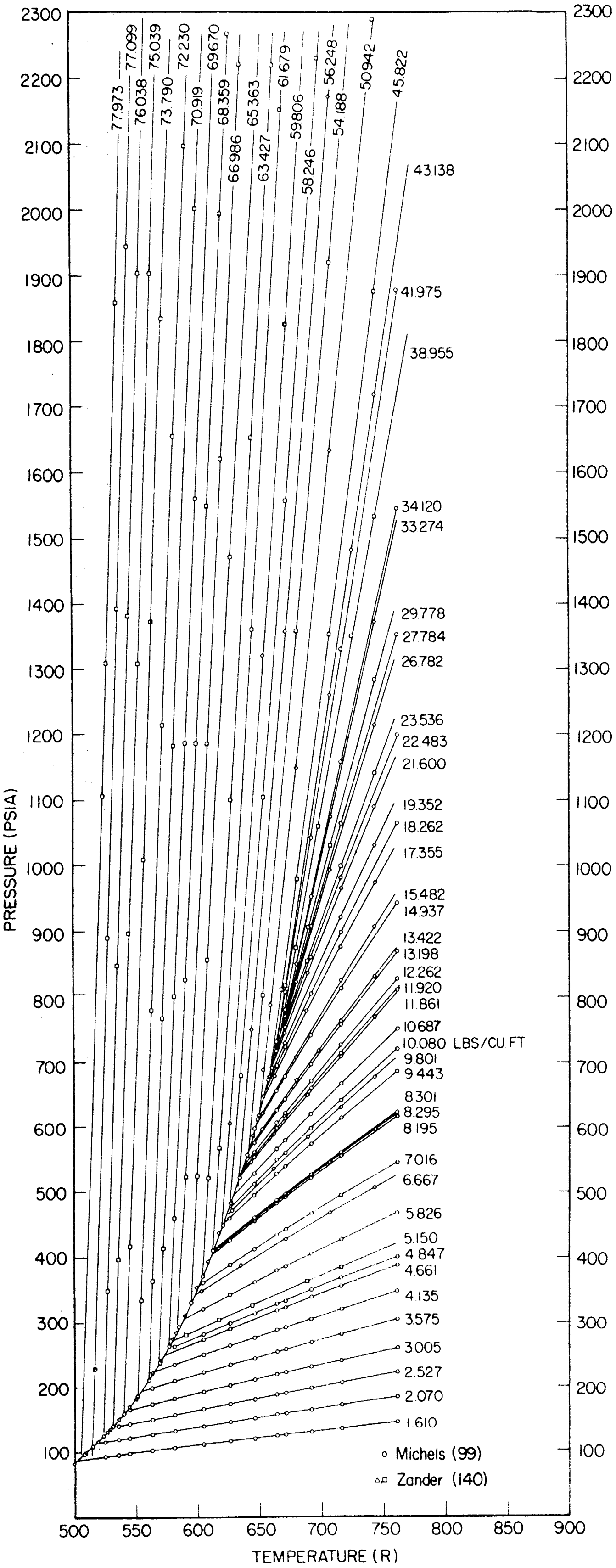

Fig. V-1. PVT behavior of chlorodifluoromethane (R-22)

Average percent deviation = -0.04%

Average absolute percent deviation = 0.11%

Standard percent deviation = 0.18%

Equation (V-1) also covers the entire isothermal PVT data reported by Zander with above deviations of 0.08, 0.23 and 0.51%, respectively. Zander's isometric data goes up to 2.34 times the critical density. This equation goes up to 1.8 times the critical density with the majority of deviations under 1% and a maximum deviation of -2.42%. Thus, we believe that the fit is extremely good.

PVT behavior of R-115 was determined by The University of Michigan (136) and Mears et al. (98). The data is presented as a P-T plot in Fig. V-2. Their data is in mutual agreement considering the experimental precision. The PVT data is fitted with Eqn. (V-1) and the constants are given in Table V-1. Also the input conditions required to evaluate these constants are given in Table V-2. Eqn. (V-1) is compared with experimental data in Tables V-17 and V-18. The correlation covered the entire range of experimental data reported in both investigations and the fit is summarized in Table V-3.

TABLE V-3

Summary of Comparison of Eqn. (V-1) with the Experimental PVT Data for R-115

Source	Average % Dev.	Average Ab.% Dev.	Standard % Dev.	Max. % Dev.
Univ. of Mich. (136)	-0.26	0.61	0.76	-2.49
Mears et al. (98)	0.18	0.29	0.41	1.03

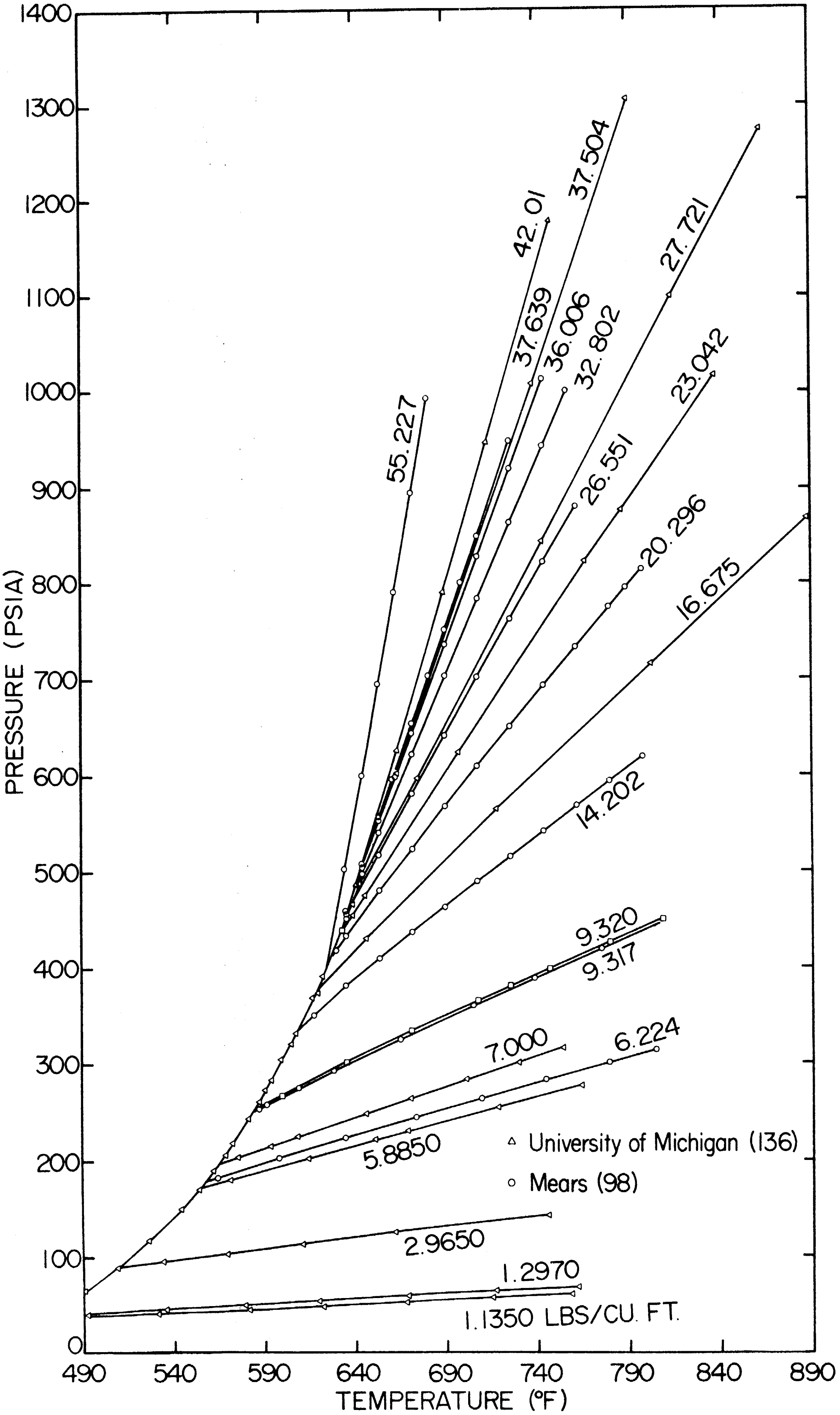

Fig. V-2. PVT behavior of chloropentafluoroethane (R-115)

Mears et al. (98) reported that their pressure values are precise to $\pm 0.2\%$, temperatures to $\pm 0.05\%$ and the volume figures are accurate to $\pm 0.1\%$.

To predict the PVT behavior of R-502 using Eqn. (V-1) given the constants for R-22 and R-115, there are two choices. The first method would be to combine the constants in Eqn. (V-1) for R-22 and R-115 as given in Table V-1, with some combining rule and then predict the PVT behavior of R-502. It was theorized that since the constants are all dimensionless, we may be able to combine them linearly on mole fraction basis. This was done and using true critical constants for the mixture, we obtained a poor fit. A more serious drawback to this method was that the equation of state for the mixture R-502 did not behave in accordance with the generalized facts, such as ,the critical isochore was not linear but the isochore around 1.4 ρ_c was. The second method was to devise a method to combine input conditions (Table V-2) for R-22 and R-115, thereby the equation of state will have the right behavior in all regions. Again it was theorized that since all the input conditions are dimensionless, we may be able to combine them linearly on a mole fraction basis. Using the input conditions thus combined and <u>true</u> critical values for R-502, we obtained an extremely good fit. This clearly indicated that if only true critical constants for the mixture can be predicted, the PVT behavior of the mixture could be predicted very confidently.

Later on a review on prediction of true or pseudocritical constants is presented and finally the methods are recommended for our mixture R-502. These methods are as follows.

In order to calculate critical volume, it was found best to combine component critical volumes linearly on mole fraction basis as proposed by Kay (63).

$$V_{cm} = x_1 V_{c1} + x_2 V_{c2} = 0.028622 \text{ ft}^3/\text{lb.} \qquad \text{(V-2)}$$

R-502 is an azeotropic minimum boiling mixture, a fact which can be asserted if the normal boiling point of the mixture is known. Thus, given the normal boiling point of the mixture, the Li, Chen and Murphy method (85b) is recommended to calculate the critical temperature.

$$\frac{T_{bm}}{T_{cm}} = x_1 \frac{T_{b1}}{T_{c1}} + x_2 \frac{T_{b2}}{T_{c2}} \qquad \text{(V-3)}$$

where

T_{bm} = boiling point of the mixture

T_{cm} = critical temperature of the mixture

T_{b1}, T_{b2} = boiling points of the components

T_{c1}, T_{c2} = critical temperatures of the mixture.

$$\therefore \; T_{cm} = 638.23 \text{ R} \qquad \text{(V-4)}$$

To calculate the critical pressure, a new method is proposed in which the reciprocals of component critical pressures are combined on mole fraction basis and it is expressed by the following equation:

$$\frac{1}{P_{cm}} = \frac{x_1}{P_{c1}} + \frac{x_2}{P_{c2}} \qquad \text{(V-5)}$$

where

P_{cm} = critical pressure of the mixture

P_{c1}, P_{c2} = component critical pressures

Using Eqn. (V-5), we obtain:

$$P_{cm} = 593.79 \text{ psia} \tag{V-6}$$

Now the critical constants being predicted, the input conditions for R-22 and R-115 are combined linearly on mole fraction basis, and are listed in Table V-2. Using these input conditions and predicted critical values, constants in Eqn. (V-1) are evaluated and listed in Table V-1. This equation is compared with the experimental PVT data of R-502 in Table V-19.

The results in Table V-19 may be compared with those in Table IV-13 along with the input conditions listed in Table V-2. The input conditions for the best correlation of Table IV-13 and those of this correlation are almost the same except for the critical values. The predicted critical temperature differs from the true value by 1.33 R or by about 0.2%. True critical pressure differs from the predicted value by 2.79 psia or by 0.47%. The predicted critical volume exceeds the true value by 0.000051 cu.ft./lb or by about 0.18%. Since the predicted critical pressure is high, the pressure values around the critical point on the real critical isotherm (T = 639.56), are high. Again, this same effect is carried to the compressed liquid region where higher pressures are predicted. Around T_R = 1.04 and 1.11, pressures are predicted within 2% except at the highest densities. Comparison of the last run at $T_R = 1.116$ was a little poor. Thus, the comparisons can be summarized as follows.

Using the method of prediction described above, we would obtain pressure values within 3% up to densities of 1.4 P_c and temperatures of 1.11 T_R except near the critical region.

This analysis may be compared with the best correlation given in Table IV-13. Input conditions for both comparisons are almost the same except for the critical constants. It may be added that if we use the exact input conditions for the best correlation with the predicted critical constants, comparisons do not improve. Finally, other predicted critical constants were used and no superior correlation was found.

Vapor Pressure

Vapor pressure values are correlated by the Martin, Kapoor and Shinn equation (93) which is as follows:

$$\ln P = A + \frac{B}{T} + C\ln T + DT + \frac{E(F-T)}{FT} \ln(F-T) \qquad \text{(V-7)}$$

where

p = pressure, psia

T = absolute temperature, R

A,B,C,D,E,F = constants of the equation

Method of evaluating these constants is illustrated with respect to R-115 data in Appendix G. Martin and Hou (91) reported that reduced pressures can be expressed as a function of $1/T_R$ and a parameter M.

Therefore, Eqn. (V-7) was transformed into reduced form as follows:

Let $$\ln P_R = A' + \frac{B'}{T_R} + C'\ln T_R + DT_R + \frac{E(F-T_R)}{FT_R}\ln(F-T_R) \qquad \text{(V-8)}$$

where $P_R = P/P_c$ = reduced pressure

$T_R = T/T_c$ = reduced temperature

A', B', C', D', E', F' = constants of the equation

The relation between the constants of Eqn. (V-8) and Eqn. (V-7) are given below:

$$A' = A - \ln P_c - \frac{E}{F}\ln T_c + C\ln T_c \qquad \text{(V-9)}$$

$$B' = (B + E\ln T_c)/T_c \qquad \text{(V-10)}$$

$$C' = C \qquad \text{(V-11)}$$

$$D' = DT_c \qquad \text{(V-12)}$$

$$E' = E/T_c \qquad \text{(V-13)}$$

$$F' = F/T_c \qquad \text{(V-14)}$$

These reduced constants may then be combined according to M factors to obtain vapor pressure of the mixture. Factor M is defined by the following equation:

$$M = M' + \frac{4}{M'} \qquad \text{(V-15)}$$

where

$$M' = \frac{T_B}{T_c - T_B}\ \ln P_c \qquad \text{(V-16)}$$

T_B = boiling temperature, R

T_c = critical temperature, R

P_c = critical pressure in atmospheres

The combining rule for the mixture may be expressed as follows:

$$G_m = G_1 \frac{|M_m - M_1|}{|M_1 - M_2|} + G_2 \frac{|M_m - M_2|}{|M_1 - M_2|} \qquad \text{(V-17)}$$

where

G_m = a typical constant in Eqn. (V-8) for the mixture

G_1, G_2 = component constants

M_m = factor M for the mixture

M_1, M_2 = factor M for the components

This is the theory used in predicting vapor pressure of R-502.

Vapor pressure of R-22 has been determined by several investigators (12,17,46,80,83,140). All the available data is plotted in Fig. V-3 and correlated by Eqn. (V-7) by Martin (46) which were reduced using Eqns. (V-9) through (V-14) and are listed in Table V-4. Comparisons of Eqn. (V-8) with the available vapor pressure values are given in Tables V-20 through V-24. A summary of these comparisons is given in Table V-5.

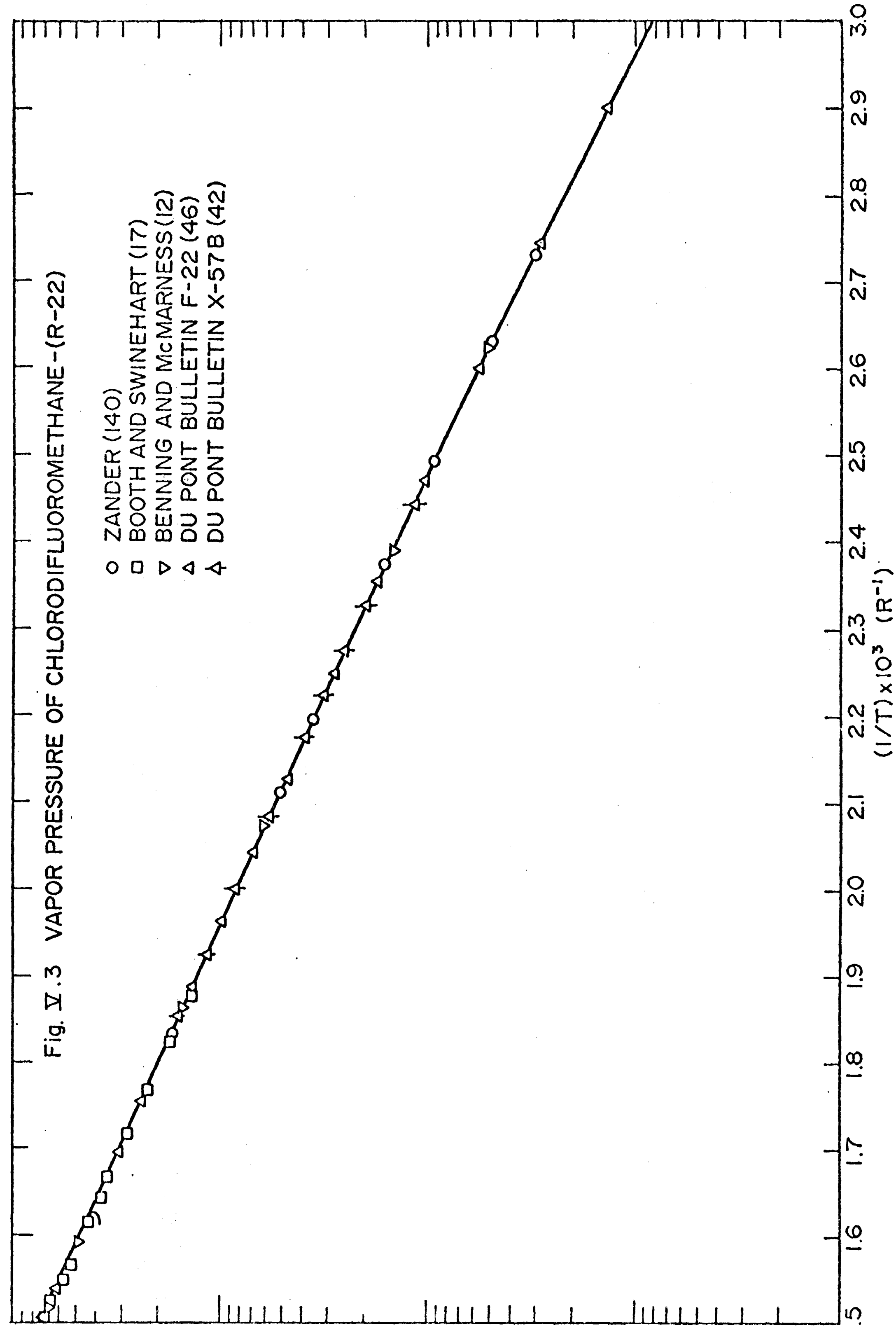

Fig. V.3 VAPOR PRESSURE OF CHLORODIFLUOROMETHANE-(R-22)

TABLE V-4

Constants in the Vapor Pressure Eqn. (V-8) and Properties of R-22, R-115 and R-502

Constant	R-22	R-115	R-502*	R-502**
T_c(R)	664.5	635.56	638.23	639.56
T_B(R)	418.33	421.99	409.92	409.92
M	7.222	7.376	7.243	7.201
P_c(psia)	721.906	456.0	593.79	591.0
A'	7.0302613	5.8980259	6.8758664	15.245786
B'	-10.33303	-11.436969	-10.483569	-7.825343
C'	-7.8610306	-10.497277	-8.2205167	0.36983496
D'	3.3522815	5.5504768	-3.6520337	-2.5717487
E'	0.46023576	0.15040074	0.41798577	0.83454005
F'	1.02	1.02	1.02	1.02

* Values given by the prediction method
** Values obtained for best data correlation

TABLE V-5

Summary of Comparisons of Eqn. (V-8) with the
Vapor Pressure Values for R-22

Source	Average % Dev.	Av. Absolute % Dev.	Max % Dev.
Booth and Swinehart (17)	-1.69	1.90	-4.47
Benning and McHarness (12)	0.35	0.49	0.99
Du Pont (46)	0.05	0.05	0.11
Downing (42)	0.59	0.59	0.89
Zander (140)	0.12	0.19	-0.47

Values reported by Zander (140) agree very well with the values reported by Du Pont (46). The poorest agreement is found with the data of Booth and Swinehart (17). The reasons for these diagreements can be determined if the impurities in the sample are accurately determined. Eqn. (V-8) predicts data of Benning and McHarness (12) within ±0.5% which is within their experimental precision. Thus the fit with Eqn. (V-8) is considered good.

Vapor pressure of R-115 was determined by several investigators (4,87,98,136) and the available values are presented in Fig. V-4. The data is correlated with Eqn. (V-7) and the constants are reduced for use in Eqn. (V-8). The reduced constants are listed in Table V-4. The correlating equation (V-8) is compared with the reported vapor pressure values in Tables V-25 through V-28, and the summary of these comparisons is given in Table V-6.

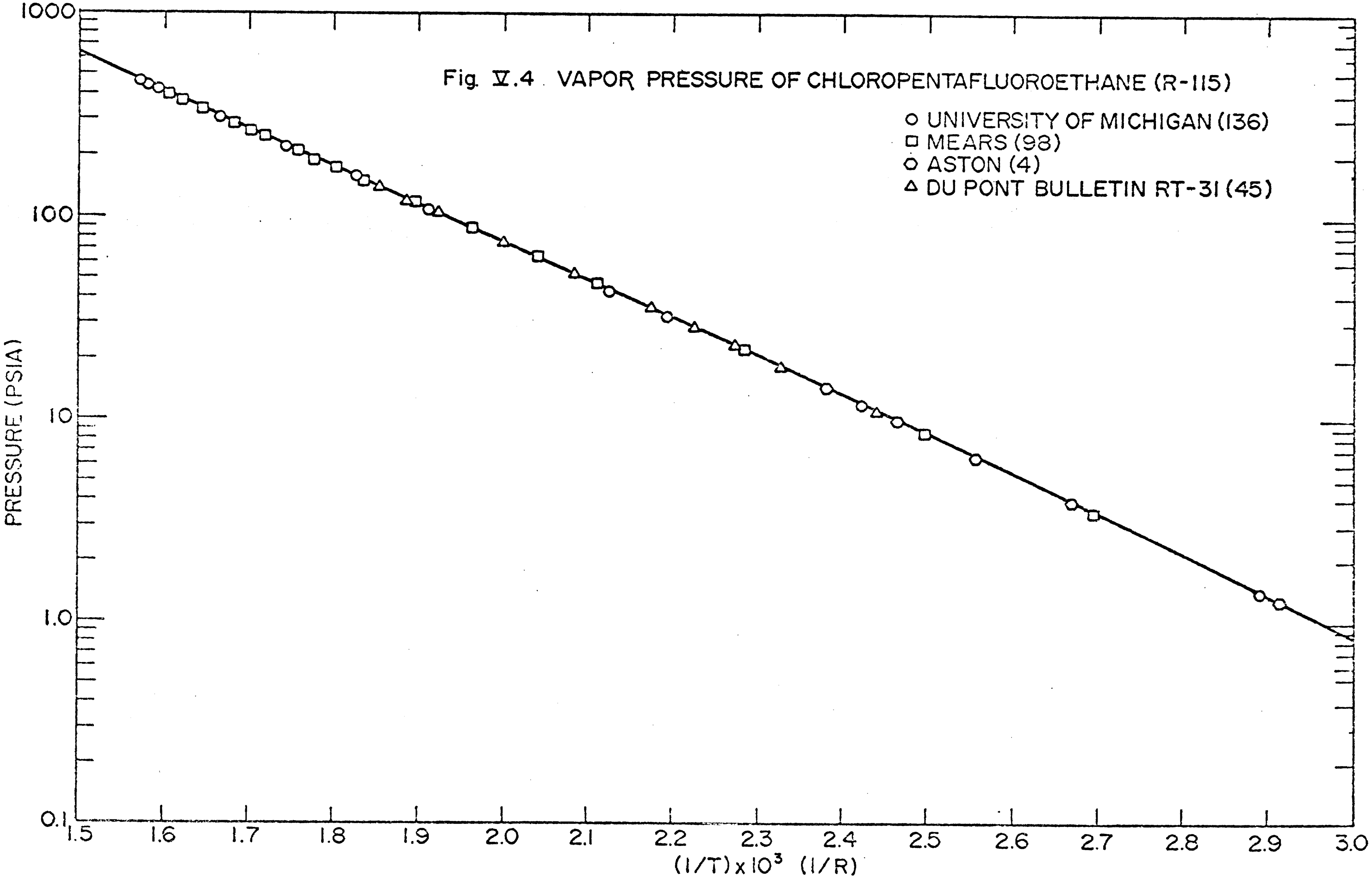

Fig. V.4 VAPOR PRESSURE OF CHLOROPENTAFLUOROETHANE (R-115)

TABLE V-6

Summary of Comparisons of Eqn. (V-8) with the Vapor Pressure Values for R-115

Source	Average % Dev.	Av. Absolute % Dev.	Max. % Dev.
Univ. of Mich.(136)	-0.51	0.70	-1.69
Mears et al. (98)	+0.19	0.56	1.48
Aston et al. (4)	0.75	0.75	1.09
Downing (42)	-1.16	1.16	-1.35

The sample of R-115 used in the vapor pressure determinations at The University of Michigan (136) contained about 0.0032% air in the vapor. The experimental precision is not reported. Aston et al. (4) used about 99.99% pure R-115 and the experimental precision is undetermined. Mears et al. (98) used 99.9 mol% pure R-115 and report that pressure measurements were precise to ±0.2% and temperature measurements were good to ±0.05. The correlating Eqn. (V-8) does predict vapor pressure values of Mears et al. (98) within the experimental precision. It is believed that the values reported by Downing are synthetic and therefore may be off as much as about 1.2%. Thus, the correlating Eqn. (V-8) is believed to be consistent with the experimental values.

Vapor pressure values for R-502 have been determined in this investigation and are discussed with the values reported by others in Chapter IV. Using the method of prediction, described earlier, constants of Eqn. (V-8) are evaluated on the basis of factor M and are listed in Table V-4. The method of prediction is compared with the vapor pressure values in Tables V-29 through V-33 and are summarized in Table V-7.

TABLE V-7

Summary of Comparisons of Eqn. (V-8) with the Vapor Pressure Values for R-502

Source	Average % Dev.	Av. Absolute % Dev.	Max. % Dev.
This Work	-1.57	2.21	7.54
Badylkes (5,6,7)	-0.14	0.74	1.74
Loffler (86)	2.47	2.47	3.93
Downing (42)	-1.35	1.39	-3.78
Du Pont (47)	-1.24	1.56	-4.48

Table V-7 must be compared with Table IV-1 where summary of the best correlation made by Martin and Downing (90) is given. In each case the average deviations are poorer for our method of prediction. The merit of this method may be seen by studying Tables V-29 through V-33 which point out that vapor pressure values are predicted within 1% in the middle ranges but as we go towards critical value and to low pressures, the deviations increase.

The reason for these differences was traced to Eqn. (V-8) where after combining the constants, at $T_R = 1$, Eqn. (V-8) for R-502 predicted a reduced pressure of 1.028. Besides the low predicted critical temperature along with high critical pressure prediction of higher pressures near the critical point. If the mixture equation is normalized to predict $P_R = 1$ at $T_R = 1$, the low pressure values would automatically fall into line since the vapor pressure line will move up accordingly.

Other methods of prediction were tried without success.

Saturated Liquid Density

Saturated liquid density values are correlated by the Martin-Hou equation (92) which is given below:

$$d_s = A + B(1-T_R)^{1/3} + C(1-T_R)^{2/3} + D(1-T_R) + E(1-T_R)^{4/3} \qquad \text{(V-18)}$$

where

d_s = density of the saturated liquid

$A = d_c$ = critical density

$T_R = T/T_c$ = reduced temperature

B,C,D,E = constants of the equation

The method of evaluation of these constants is illustrated with the data for R-115 in Appendix H. Equation (V-18) can be written in the reduced form as follows:

$$\frac{d_s}{d_c} = 1 + B'(1-T_R)^{1/3} + C'(1-T_R)^{2/3} + D'(1-T_R) + E'(1-T_R)^{4/3} \qquad \text{(V-19)}$$

where

$B' = B/d_c$

$C' = C/d_c$

$D' = D/d_c$

$E' = E/d_c$

Eqn. (V-19) may now be used to predict the mixture saturated liquid densities by combining the reduced parameters linearly on mole fraction basis.

TABLE V-8

Constants in the Saturated Liquid Density Eqn. V-19
For R-22, R-115 and R-502

Constant	R-22	R-115	R-502*	R-502**
T_c(R)	664.5	635.56	638.23	639.56
d_c(lbs/cuft)	32.76	37.3	34.938	35.0
B'	1.667717	1.761663	1.702477	1.528125
C'	1.121762	1.066756	1.101410	1.824690
D'	-0.680481	-1.270241	-0.898692	-2.002303
E'	0.624948	1.168901	0.826210	1.385114

* Values given by the prediction method
**Values obtained for best data correlation

Saturated liquid density values for R-22 have been reported in the literature (14,46,140) and constants in correlating Eqn. (V-18) have been reported by Du Pont (46). The data is presented in Fig. IV-2 with the location of the rectilinear diameter. Fig. IV-2 confirms the value of the critical density of R-22 to be 32.76 lbs/cu.ft. Constants in Eqn. (V-18) are reduced for use in Eqn. (V-19) and are listed in Table V-8. The comparisons of the correlating Eqn. (V-19) with the reported saturated liquid density values are given in Tables V-34 to V-36 and are summarized in Table V-9.

TABLE V-9

Summary of Comparisons of Eqn. (V-19) with the Saturated Liquid Density Values for R-22

Source	Average % Dev.	Av. Absolute % Dev.	Max. % Dev.
Benning and McHarness (14)	-0.004	0.044	-0.08
Du Pont (46)	-0.003	0.003	-0.02
Zander (140)	-0.16	0.17	-0.29

Benning and McHarness (14) report a precision in temperature measurement of ±0.1 C amounting to an error of about ±0.01%. The precision of density measurements was not given. Since Eqn. (V-19) given by Du Pont (46) was based on this data, the agreement is obvious. Besides values reported by Du Pont (46) are calculated from Eqn. (V-19) and hence the fine agreement is obtained as indicated in Table V-9. Zander's (140) saturated liquid density values are consistently lower except near the critical. He reports a precision in the density measurement of ±0.01%. Thus, Eqn. (V-19) does not predict Zander's (140) data within his experimental precision but is off by about -0.06%.

Saturated liquid density of R-115 was determined at The University of Michigan (136) and by Mears et al. (98). The data is plotted in Fig. IV-2. The rectilinear diameter confirms the value of critical density of 37.3 lbs/cu.ft. The experimental data is correlated by Eqn. (V-18) and constants are reduced for use in Eqn. (V-19) which are listed in Table V-8. Comparisons of Eqn. (V-19) with the experimental saturated liquid density values are presented in Table V-37 and Table V-38, and a summary is presented in Table V-10.

TABLE V-10

Summary of Comparisons of Eqn. (V-19) with the Saturated Liquid Density Values for R-115

Source	Average % Dev.	Av. Absolute % Dev.	Max. % Dev.
Univ. of Mich. (136)	-0.004	0.25	0.547
Mears et al. (98)	-0.05	0.27	0.716

Mears et al. (98) report a volume precision of ±0.1% and temperature precision of ±0.05%. Experimental precision of The University of Michigan (136) values is believed to be less than ±0.1% for density values.

Saturated liquid density of R-502 is determined in this work and along with other values is discussed in Chapter IV. Using the method of prediction, as described above, constants in Eqn. (V-19) were evaluated and are listed in Table V-8. The comparisons of Eqn. (V-19) with saturated liquid density values are presented in Tables V-39 through V-42 and are summarized in Table V-11.

TABLE V-11

Summary of Comparisons of Eqn. (V-19) with the Saturated Liquid Density Values for R-502

Source	Average % Dev.	Av. Absolute % Dev.	Max. % Dev.
This Work	0.29	0.44	2.9
Badylkes (5,6,7)	1.06	1.06	1.95
Loffler (86)	0.51	0.51	6.13
Du Pont (47)	1.91	1.91	5.51

Table V-11 may be compared with Table IV-2. Values reported by Du Pont (47) and Badylkes (5,6,7) are predicted better than before while the values of this work and Loffler are predicted with little larger deviations. To see the fit, one must examine the comparison of Tables V-39 through V-42 . Eqn. (V-19) predicts the experimental data of this work within 0.2% for most of the points up to a reduced temperature of 0.96. The difficulty occurs near the critical point because of the fact that predicted critical density is lower than the true value and likewise predicted critical temperature is lower than the true value. Similar observations can be made on the saturated liquid density values reported by others. Thus, this method of prediction of saturated liquid density values may be used with confidence up to 0.97 T_R.

To complete the data analysis equations for the rectilinear diameters of R-22 and R-115 are also formulated. The equations are given below and compared with the rectilinear diameter values in Tables V-43 and V-44.

For R-22 $$d = 32.76 + 30.129\ (1-T/664.5) \qquad (V\text{-}20)$$

For R-115 $$d = 37.30 + 32.834\ (1-T/639.56) \qquad (V\text{-}21)$$

Critical Constants

In our analysis of prediction of properties of the mixture R-502 from the properties of its components, we found that if true critical constants are used then the constants of analytical equations, describing certain property, may be combined simply on mole fraction basis. Several methods are available in the literature for the prediction of critical constants. Some methods are formulated to predict pseudocritical constants which can be used in general correlations. Other methods predict the true critical constants. A few of these methods are described in Appendix J. They are all summarized in Table V-12.

Some methods simply use the component critical constants and the mole or mass fractions in the mixture. Other methods employ extra parameters such as accentric factor, molal average boiling points, etc. Our mixture is a minimum boiling point azeotrope and this fact could be determined only if the normal boiling point of the azeotrope is measured and compared with the component boiling points. Thus, it is

TABLE V-12

Summary of Mixing Rules for Critical Constants of R-502

Method #	Reference	P_{cm} psia	T_{cm} R	V_{cm} ft^3/lb	Z_{cm}
I.	Kay-Mole fraction	623.52	653.8	0.028622	0.2705
II.	Kay-Mass fraction	585.76	649.69	0.028622	0.2721
III.	Geometric Mean Av.	616.4	653.7	0.02827	0.2708
IV.	Lorentz Cube Root Av.	618.6	653.85	0.028388	0.2708
V.	Chueh & Prausnitz - Simplified (34a)	-	647.81	0.028622	-
VI.	Chueh & Prausnitz (34b)	-	651.70	0.029590	-
VII.	Ekiner & Thodos (47a)	-	661.2	-	-
VIII.	Grieves & Thodos (52a)	-	650.78	-	-
IX.	Leland-Mueller (84a)	600.0	655.0	0.028388	0.2705
X.	Joffe-Method A (67a)	598.2	645.53	-	-
		583.7	639.56*	-	-
		578.4	639.98	-	-
XI.	Joffe-Method B (67a)	597.4	649.98	-	-
		587.8	639.56*	-	-
XII.	Li (85a)	-	650.6	-	-
XIII.	Kreglewski & Kay (82a)	528.56	639.56*	-	-
XIV.	Li,Chen & Murphy (85b)	-	638.23	-	-
XV.	This Work	593.79	-	-	-
True Values		591.0	639.56	0.028571	0.2747

*True values of T_{cm} were substituted in the equations.

believed that having a knowledge of the normal boiling point of the mixture is necessary, and as proven below, a sufficient condition to be able to predict the critical constants of the mixture. Based on this reasoning, we recommend the Li, Chen and Murphy (85b) method for the prediction of critical temperature. From Table V-12 it may be observed that this method is extremely superior to other methods of prediction and predicts the true critical temperature of R-502 within 1.33 F.

Averaging the molal critical volumes on mole fraction yields, the critical volume for the mixture is within 0.000051 ft^3/lb or within 0.18%. Other methods deviate by larger amounts.

In order to predict the critical pressure of the mixture, we were looking for a simple method. Mass fraction averaging gives a fairly good value of the critical pressure. Then Joffe's (67a) methods are best for this prediction. In order to use Joffe's method (67a) we have to use the critical temperatures predicted by his method which differ from the true value by about 6 R for his simple method and by about 10 R for his second method. But considering all the combinations of T_{cm} and P_{cm} predicted by different methods, Joffe's method-A (67a) is simple and the best.

We were not happy with the fact that to use Joffe's (67a) method A, even though the critical pressure is predicted within the precision of its determinations, the predicted critical temperature differed from the true value by a large amount. Further investigations proved successful and we are proposing a new and simple method for the prediction of critical temperature which is described by Eqn. (V-5) given below:

$$\frac{1}{P_{cm}} = \frac{x_i}{P_{c1}} + \frac{x_2}{P_{c2}} \qquad \text{(V-5)}$$

The reasoning behind formulating Eqn. (V-5) was based on the fact that we do need the boiling point of the mixture to predict its critical temperature. Eqn. (V-3) describes the method of prediction of critical temperature:

$$\frac{T_{Bm}}{T_{cm}} = x_1 \frac{T_{b1}}{T_{c1}} + x_2 \frac{T_{b2}}{T_{c2}} \qquad \text{(V-3)}$$

Let us substitute the pressures corresponding to temperatures in Eqn. (V-3). At the boiling points pressure is atmospheric (14.7 psia). At the critical temperatures the pressures are critical. Therefore, Eqn. (V-3) becomes:

$$\frac{14.7}{P_{cm}} = x_1 \frac{14.7}{P_{c1}} + x_2 \frac{14.7}{P_{c2}} \qquad \text{(V-22)}$$

Cancelling the common factor 14.7 in Eqn. (V-22) we obtain our new method of prediction of critical pressure of a mixture. As stated above, this method predicts a critical value for the mixture of 593.79 psia which is within 2.79 psia of the true value or within 0.47%.

In summary, we have three methods which predict the critical constants of R-502 very well compared to other methods.

Intermolecular Potential Energy

A general nature of the potential energy of interaction between two molecules is presented in Fig. II-8. Several methods to describe this curve are reviewed in Chapter II. Most of the methods can be characterized by the number of adjustable parameters they contain and the higher this number, the more difficult the method. We were looking for a simple method containing a few parameters which can be handled mathematically and still be realistic. Our investigation started with the two parameter Lennard-Jones (12-6) potential and ended up with multiparameter method of Boys and Sharitt (18,19,20) where computers have to be used. In the simplest method due to Lennard-Jones (12-6) the two parameters are determined by either trial and error method or graphically, involving extensive calculations. Therefore a new method is proposed to obtain two characteristic parameters d_m and U_m. This method is described in detail in Appendix K. Only important features are discussed here.

The second virial coefficient is given in terms of the intermolecular potential energy by the following equation:

$$B = 2\pi N \int_{o}^{\infty} (e^{-U_m/kT} - 1)\, r^2 dr \qquad \text{(V-23)}$$

As discussed in Appendix K, a new equation is proposed for the intermolecular potential energy:

$$U = 4U_m \left[\left(\frac{d_o}{r}\right)^{12} - \left(\frac{d_o}{r}\right)^{6} \right] \qquad \text{for } d_o < r < \infty \qquad \text{(V-24)}$$

and

$$e^{-U/kT} = Cr^{12} \qquad \text{for } 0 < r < d_o \qquad \text{(V-25)}$$

Further, an assumption is made that in the region beyond d_o we may express the exponential term in terms of quadratic expansion as follows:

$$e^{-U/kT} = 1 - U/kT + 1/2\ (U/kT)^2 \qquad \text{(V-26)}$$

Final expression for the second virial coefficient is given below:

$$B = 8\pi N\ d_o^3\ [\frac{1}{15} + \frac{2}{9}\ \frac{U_m}{kT} - \frac{16}{315}\ (\frac{U_m}{kT})^2] \qquad \text{(V-27)}$$

The parameters d_o and U_m are the characteristic parameters.

In correlating PVT data we used several input conditions out of which three pertained to the second virial coefficient. The second virial coefficient at the Boyle temperature is zero. Two values of generalized second virial coefficient at $T_R = 1.0$ and $T_R = 0.8$ are used as other input conditions. Given B = 0, Eqn. (V-27) can be easily solved for U_m/k and from a value of B at $T_R = 1.0$, second parameter d_o can be determined. To see the reasonableness of this procedure values of U_m and d_o could be used to predict B at $T_R = 0.8$. Using this procedure, the parameters U_m and d_o for R-22 and R-115 were evaluated and they are listed in Table V-13.

Order of magnitude of these parameters is comparable to generalized correlations (Table V-13). Thus our approximations are reasonable.

Going further to predict the second virial coefficients for R-502, we combined the component parameters as follows:

$$d_{o_{12}} = (d_{o_1} + d_{o_2})/2 \qquad \text{(V-28)}$$

$$U_{m_{12}} = (U_{m_1} U_{m_2})^{1/2} \qquad \text{(IV-29)}$$

Using the relationship between the second virial coefficient of mixtures with those of components, the mixture values were predicted and they are summarized in Table K-1.

From the input condition to the equation of state for R-502, at the Boyle temperature a value of B_{12} was calculated to be - 3.58 cc/gmole. Using the parameters calculated by Eqns. (V-28) and (V-29), the predicted value was +3.02 cc/gmole or within a 0.6 cc/gmole. At another temperature (T_R = 1 for R-502), value of B_{12} was calculated to be -241.09 and the predicted value is -251.53 cc/gmole. Similarly a disagreement of about 10 cc/gmole was obtained at T_R = 0.8 for R-502. These disagreements may be compared with the experimentally determined second virial coefficients by two different sources, where differences as high as 10 cc/gmole are usually observed. Thus using the component parameters evaluated by this new method, then using well known combining rules we have been able to predict the second virial coefficient for the mixture reasonably well.

TABLE V-13

Summary of Intermolecular Potential Energy Parameters

Parameter	R-22	R-115	R-502
U_m/k (K)	-239.3 *	-228.9 *	-230.33 *
d_o (Å)	5.24*	5.98 *	5.51 *
d_m (Å)	5.88	6.71	6.18
U_m(erg)x10^{16}	330.3	316.0	318.0
V_c(cc/g)	1.906	1.674	1.784
V_c/d_m^3	1.346	1.421	1.401
T_c(K)	369.17	353.09	355.31
kT_c/U_m	1.543	1.543	1.543
$P_c d_m^3/U_m$	0.3063	0.3005	0.3024
$P_c V_c/kT_c$	0.2672	0.2769	0.2747

$k = 1.38044 \times 10^{16}$ erg/deg

1 atm $= 1.0133 \times 10^{6}$ dynes/sq.cm.

*These characteristic parameters can be used in the Lennard-Jones potential energy equation II-48, even though they were derived specifically for equations V-24 and V-25.

If the Boyle temperature is not used, two values of B will give a quadratic in U_m/k which can be easily solved exactly and then d_o could be determined. This is the advantage of this method.

Also considering R-502 to be a pure substance, parameters d_o and U_m were evaluated and are given in Table V-13. Generalized parameters are also calculated.

In summary, we have been able to predict the PVT behavior, vapor pressure, saturated liquid density using simple combination rules for equation constants and critical constants. Using a new analytical method of determining the intermolecular potential energy parameters, we were able to predict the second virial coefficient of the mixture from the component values.

TABLE V-14

V-14. Comparison of Eqn. V-1 and PVT Data for R-22 Reported by Michels (99)

V/0.030525	T/664.5	$P_{exp}/721.906$	$P_{calc}/721.906$	%Dev.
20.348239	0.791	0.130	0.130	-0.08
20.348239	0.808	0.133	0.133	-0.02
20.348239	0.821	0.136	0.136	0.01
20.348239	0.848	0.142	0.142	0.04
20.348239	0.875	0.147	0.147	0.06
20.348239	0.911	0.154	0.154	0.05
20.348239	0.943	0.161	0.161	0.04
20.348239	0.973	0.167	0.167	0.03
20.348239	1.000	0.173	0.173	0.03
20.348239	1.011	0.175	0.175	0.01
20.348239	1.042	0.181	0.181	0.00
20.348239	1.079	0.188	0.188	0.01
20.348239	1.146	0.201	0.202	-0.03
15.828337	0.791	0.161	0.161	-0.17
15.828337	0.808	0.166	0.166	-0.08
15.828337	0.821	0.169	0.169	-0.05
15.828337	0.848	0.177	0.177	0.01
15.828337	0.875	0.184	0.184	0.04
15.828337	0.911	0.194	0.194	0.05
15.828337	0.943	0.203	0.203	0.05
15.828337	0.973	0.211	0.210	0.03
15.828337	1.000	0.218	0.218	0.00
15.828337	1.011	0.220	0.220	-0.00
15.828337	1.042	0.229	0.229	-0.01
15.828337	1.079	0.238	0.238	-0.01
15.828337	1.146	0.256	0.256	-0.05
12.963473	0.808	0.195	0.196	-0.18
12.963473	0.821	0.200	0.200	-0.11

TABLE V-14 (contd.)

12.963473	0.848	0.210	0.210	-0.02
12.963473	0.875	0.219	0.219	0.03
12.963473	0.911	0.231	0.231	0.04
12.963473	0.943	0.242	0.242	0.03
12.963473	0.973	0.252	0.252	0.03
12.963473	1.000	0.261	0.261	0.01
12.963473	1.011	0.264	0.264	0.00
12.963473	1.042	0.275	0.275	-0.02
12.963473	1.079	0.286	0.287	-0.02
12.963473	1.146	0.308	0.308	-0.07
10.902211	0.821	0.230	0.231	-0.21
10.902211	0.848	0.242	0.242	-0.08
10.902211	0.875	0.253	0.253	-0.01
10.902211	0.943	0.281	0.281	0.03
10.902211	0.911	0.268	0.268	0.02
10.902211	0.973	0.293	0.293	0.02
10.902211	1.000	0.304	0.304	0.01
10.902211	1.011	0.308	0.308	-0.01
10.902211	1.042	0.321	0.321	-0.02
10.902211	1.079	0.335	0.335	-0.03
10.902211	1.146	0.361	0.362	-0.08
9.162981	0.848	0.277	0.277	-0.18
9.162981	0.875	0.291	0.291	-0.06
9.162981	0.911	0.309	0.309	-0.00
9.162981	0.943	0.326	0.325	0.01
9.162981	0.973	0.340	0.340	0.01
9.162981	1.000	0.354	0.354	-0.00
9.162981	1.011	0.359	0.359	-0.00
9.162981	1.042	0.374	0.374	-0.02
9.162981	1.079	0.391	0.391	-0.05

TABLE V-14 (contd.)

9.162981	1.146	0.423	0.424	-0.10
7.922686	0.875	0.325	0.326	-0.14
7.922686	0.911	0.347	0.347	-0.03
7.922686	0.943	0.366	0.366	-0.00
7.922686	0.973	0.384	0.384	0.00
7.922686	1.000	0.400	0.400	-0.00
7.922686	1.011	0.406	0.406	-0.01
7.922686	1.042	0.424	0.424	-0.03
7.922686	1.079	0.444	0.444	-0.06
7.922686	1.146	0.482	0.482	-0.11
7.028337	0.911	0.380	0.380	-0.09
7.028337	0.943	0.402	0.402	-0.02
7.028337	1.000	0.441	0.441	-0.02
7.028337	1.011	0.448	0.448	-0.02
7.028337	1.042	0.468	0.468	-0.04
7.028337	1.079	0.492	0.492	-0.07
7.028337	1.146	0.535	0.536	-0.09
6.759378	0.875	0.365	0.366	-0.28
6.759378	0.911	0.391	0.391	-0.10
6.759378	0.943	0.414	0.415	-0.03
6.759378	0.973	0.436	0.436	-0.05
6.759378	1.000	0.455	0.455	-0.01
6.759378	1.011	0.462	0.462	-0.02
6.759378	1.042	0.484	0.484	-0.03
6.759378	1.079	0.508	0.509	-0.06
6.759378	1.146	0.554	0.554	-0.11
5.623260	0.911	0.444	0.445	-0.22
5.623260	0.943	0.474	0.475	-0.09
5.623260	0.973	0.501	0.501	-0.03
5.623260	1.000	0.525	0.525	-0.03

TABLE V-14 (contd.)

5.623260	1.011	0.534	0.534	-0.03
5.623260	1.042	0.560	0.561	-0.05
5.623260	1.079	0.591	0.592	-0.07
5.623260	1.146	0.648	0.648	-0.11
4.669615	0.911	0.499	0.501	-0.43
4.669615	0.943	0.537	0.538	-0.19
4.669615	0.973	0.571	0.571	-0.08
4.669615	1.000	0.601	0.601	-0.05
4.669615	1.011	0.612	0.613	-0.04
4.669615	1.042	0.646	0.646	-0.04
4.669615	1.079	0.684	0.685	-0.08
4.669615	1.146	0.755	0.755	-0.12
3.997379	0.943	0.589	0.591	-0.31
3.997379	0.973	0.631	0.631	-0.13
3.997379	1.000	0.668	0.668	-0.06
3.997379	1.011	0.681	0.682	-0.06
3.997379	1.042	0.722	0.722	-0.04
3.997379	1.079	0.769	0.769	-0.06
3.997379	1.146	0.853	0.854	-0.12
3.946601	0.973	0.637	0.636	0.06
3.946601	1.000	0.673	0.674	-0.09
3.946601	1.011	0.687	0.687	-0.08
3.946601	1.042	0.728	0.729	-0.06
3.946601	1.079	0.776	0.776	-0.09
3.946601	1.146	0.861	0.863	-0.16
3.469287	0.943	0.635	0.638	-0.49
3.469287	0.973	0.685	0.686	-0.20
3.469287	1.000	0.729	0.730	-0.08
3.469287	1.011	0.745	0.746	-0.06
3.469287	1.042	0.794	0.794	-0.04

TABLE V-14 (contd.)

3.469287	1.079	0.850	0.850	-0.05
3.469287	1.146	0.951	0.952	-0.10
3.250123	0.973	0.709	0.710	-0.24
3.250123	1.000	0.757	0.758	-0.09
3.250123	1.011	0.775	0.775	-0.06
3.250123	1.042	0.828	0.828	-0.03
3.250123	1.079	0.888	0.888	-0.03
3.250123	1.146	0.997	0.998	-0.10
3.065356	0.973	0.730	0.731	-0.25
3.065356	1.000	0.782	0.782	-0.09
3.065356	1.011	0.801	0.801	-0.06
3.065356	1.042	0.858	0.858	-0.00
3.065356	1.079	0.923	0.923	-0.02
3.065356	1.146	1.041	1.041	-0.09
2.748239	0.973	0.766	0.769	-0.36
2.748239	1.000	0.826	0.827	-0.10
2.748239	1.011	0.849	0.849	-0.05
2.748239	1.042	0.914	0.914	0.03
2.748239	1.079	0.989	0.989	0.03
2.748239	1.146	1.124	1.124	-0.05
2.671712	0.973	0.775	0.778	-0.37
2.671712	1.000	0.838	0.838	-0.09
2.671712	1.011	0.861	0.861	-0.03
2.671712	1.042	0.929	0.928	0.05
2.671712	1.079	1.006	1.006	0.07
2.671712	1.146	1.146	1.146	-0.02
2.482228	0.973	0.796	0.800	-0.50
2.482228	1.000	0.866	0.866	-0.10
2.482228	1.011	0.891	0.891	-0.03
2.482228	1.042	0.966	0.965	0.08

TABLE V-14 (contd.)

2.482228	1.079	1.051	1.050	0.08
2.482228	1.146	1.204	1.204	-0.00
2.193284	0.973	0.826	0.831	-0.61
2.193284	1.000	0.908	0.909	-0.08
2.193284	1.011	0.938	0.938	0.03
2.193284	1.042	1.026	1.024	0.17
2.193284	1.079	1.126	1.123	0.22
2.193284	1.146	1.305	1.304	0.12
1.793939	1.000	0.962	0.962	-0.05
1.793939	1.011	1.001	1.000	0.13
1.793939	1.042	1.115	1.111	0.37
1.793939	1.079	1.244	1.239	0.42
1.793939	1.146	1.475	1.472	0.24
1.457101	1.000	0.993	0.993	-0.02
1.457101	1.011	1.044	1.042	0.24
1.457101	1.042	1.191	1.185	0.51
1.457101	1.079	1.360	1.352	0.54
1.457101	1.146	1.662	1.657	0.35
1.179099	1.000	1.003	1.002	0.00
1.179099	1.011	1.067	1.065	0.21
1.179099	1.042	1.256	1.252	0.30
1.179099	1.079	1.475	1.470	0.30
1.179099	1.146	1.875	1.871	0.20
0.960131	1.000	1.003	1.004	-0.05
0.960131	1.011	1.081	1.085	-0.37
0.960131	1.042	1.320	1.328	-0.61
0.960131	1.079	1.606	1.614	-0.51
0.960131	1.146	2.142	2.145	-0.13
0.780475	1.000	1.013	1.013	0.00
0.780475	1.011	1.118	1.123	-0.49

TABLE V-14 (contd.)

0.780475	1.042	1.445	1.455	-0.70
0.780475	1.079	1.843	1.848	-0.27
0.780475	1.146	2.603	2.586	0.67

TABLE V-15

V-15. Comparison of Eqn. V-1 and Isometric PVT Data for R-22 Reported by Zander (140)

Density d g/cc	Temp. t C	Pressure P bars	V/0.030525	T/664.5	P_{exp}/721.906	P_{calc}/721.06	%Dev.
1.2490	18.17	76.23	0.420146	0.789	1.531	3.114	-103.35
1.2490	19.97	90.25	0.420146	0.794	1.813	3.406	-87.85
1.2490	24.62	128.21	0.420146	0.807	2.576	4.168	-61.82
1.2490	29.99	168.50	0.420146	0.821	3.385	4.941	-45.95
1.2490	35.14	208.37	0.420146	0.835	4.186	5.672	-35.48
1.2350	14.20	15.73	0.424909	0.778	0.316	1.666	-427.13
1.2350	20.28	61.33	0.424909	0.795	1.232	2.641	-114.33
1.2350	24.89	96.04	0.424909	0.807	1.930	3.345	-73.37
1.2350	29.98	134.08	0.424909	0.821	2.694	4.089	-51.79
1.2350	35.08	172.38	0.424909	0.835	3.463	4.800	-38.59
1.2350	39.83	207.84	0.424909	0.848	4.176	5.433	-30.10
1.2180	19.83	24.02	0.430839	0.794	0.483	1.673	-246.79
1.2180	24.64	58.37	0.430839	0.807	1.173	2.386	-103.43
1.2180	29.81	95.24	0.430839	0.821	1.913	3.120	-63.07
1.2180	34.87	131.31	0.430839	0.834	2.638	3.809	-44.40
1.2180	40.02	168.00	0.430839	0.848	3.375	4.482	-32.78
1.2180	44.85	202.01	0.430839	0.861	4.059	5.086	-25.32
1.2020	24.71	27.33	0.436574	0.807	0.549	1.615	-194.02
1.2020	29.78	61.72	0.436574	0.821	1.240	2.313	-86.55
1.2020	33.97	90.21	0.436574	0.832	1.812	2.871	-58.41
1.2020	40.03	131.28	0.436574	0.848	2.638	3.647	-38.27
1.2020	45.01	165.18	0.436574	0.862	3.319	4.259	-28.34
1.2020	49.84	197.62	0.436574	0.875	3.970	4.831	-21.69
1.1820	29.87	28.74	0.443961	0.821	0.577	1.434	-148.30
1.1820	36.27	69.52	0.443961	0.838	1.397	2.248	-60.96
1.1820	40.18	94.63	0.443961	0.849	1.901	2.729	-43.55
1.1820	45.16	126.54	0.443961	0.862	2.542	3.324	-30.77
1.1820	55.24	191.23	0.443961	0.890	3.842	4.472	-16.41

TABLE V-15 (contd.)

1.1570	34.89	23.01	0.453554	0.834	0.462	1.096	-137.09
1.1570	40.06	53.69	0.453554	0.848	1.079	1.707	-58.21
1.1570	45.04	83.74	0.453554	0.862	1.682	2.279	-35.44
1.1570	50.18	114.13	0.453554	0.876	2.293	2.853	-24.43
1.1570	55.30	144.64	0.453554	0.890	2.906	3.410	-17.34
1.1570	65.10	203.22	0.453554	0.916	4.083	4.435	-8.63
1.1360	40.00	25.02	0.461939	0.848	0.503	0.984	-95.69
1.1360	44.99	52.81	0.461939	0.862	1.061	1.535	-44.65
1.1360	50.07	81.61	0.461939	0.876	1.640	2.083	-27.03
1.1360	60.20	138.05	0.461939	0.903	2.774	3.139	-13.19
1.1360	65.14	164.44	0.461939	0.916	3.304	3.638	-10.12
1.1360	70.22	192.81	0.461939	0.930	3.874	4.140	-6.87
1.1160	45.02	28.54	0.470217	0.862	0.573	0.936	-63.30
1.1160	50.08	55.10	0.470217	0.876	1.107	1.462	-32.02
1.1160	55.13	81.83	0.470217	0.889	1.644	1.976	-20.17
1.1160	60.09	107.62	0.470217	0.903	2.162	2.471	-14.30
1.1160	70.15	161.14	0.470217	0.930	3.237	3.450	-6.55
1.1160	75.19	187.56	0.470217	0.944	3.768	3.927	-4.21
1.0950	49.95	31.64	0.479235	0.875	0.636	0.892	-40.38
1.0950	55.09	56.85	0.479235	0.889	1.142	1.394	-22.07
1.0950	60.11	81.81	0.479235	0.903	1.644	1.877	-14.18
1.0950	65.18	106.86	0.479235	0.916	2.147	2.357	-9.77
1.0950	71.36	137.51	0.479235	0.933	2.763	2.932	-6.13
1.0950	75.14	156.43	0.479235	0.943	3.143	3.279	-4.34
1.0950	85.04	205.87	0.479235	0.970	4.136	4.171	-0.84
1.0730	55.13	36.01	0.489061	0.889	0.723	0.890	-22.97
1.0730	65.07	81.80	0.489061	0.916	1.643	1.797	-9.32
1.0730	71.44	111.86	0.489061	0.933	2.247	2.367	-5.30
1.0730	80.30	153.24	0.489061	0.957	3.079	3.146	-2.18
1.0730	90.21	199.73	0.489061	0.984	4.013	4.000	0.32

TABLE V-15 (contd.)

1.0470	60.09	36.11	0.501206	0.903	0.725	0.832	-14.74
1.0470	65.10	59.00	0.501206	0.916	1.185	1.261	-6.40
1.0470	75.42	101.52	0.501206	0.944	2.040	2.133	-4.57
1.0470	95.02	186.52	0.501206	0.997	3.747	3.749	-0.04
1.0160	65.12	35.92	0.516498	0.916	0.722	0.763	-5.65
1.0160	75.44	75.88	0.516498	0.944	1.525	1.573	-3.18
1.0160	85.10	113.93	0.516498	0.970	2.289	2.324	-1.52
1.0160	95.03	153.14	0.516498	0.997	3.077	3.088	-0.37
1.0160	105.06	192.65	0.516498	1.024	3.871	3.853	0.45
0.9880	70.09	39.12	0.531136	0.930	0.786	0.789	-0.38
0.9880	85.26	93.85	0.531136	0.971	1.885	1.892	-0.33
0.9880	100.32	148.51	0.531136	1.012	2.984	2.977	0.22
0.9880	115.23	203.64	0.531136	1.052	4.091	4.044	1.15
0.9580	74.87	41.55	0.547769	0.943	0.835	0.821	1.65
0.9580	90.01	91.09	0.547769	0.984	1.830	1.835	-0.24
0.9580	100.38	125.90	0.547769	1.012	2.529	2.527	0.08
0.9580	120.17	192.69	0.547769	1.065	3.871	3.847	0.63
0.9330	80.06	46.66	0.562446	0.957	0.938	0.950	-1.33
0.9330	89.94	76.11	0.562446	0.984	1.529	1.566	-2.42
0.9330	100.13	107.39	0.562446	1.011	2.158	2.203	-2.08
0.9330	115.10	153.88	0.562446	1.052	3.092	3.139	-1.52
0.9330	129.95	200.54	0.562446	1.092	4.029	4.069	-0.98
0.9010	84.85	51.69	0.582422	0.970	1.039	1.019	1.84
0.9010	100.03	93.63	0.582422	1.011	1.881	1.882	-0.07
0.9010	120.21	149.80	0.582422	1.066	3.010	3.038	-0.93
0.8680	89.77	55.33	0.604565	0.983	1.112	1.111	0.05
0.8680	105.16	93.65	0.604565	1.025	1.882	1.904	-1.19
0.8680	120.10	132.47	0.604565	1.065	2.661	2.681	-0.73
0.8680	140.09	184.98	0.604565	1.119	3.716	3.729	-0.35
0.8160	89.96	47.43	0.643091	0.984	0.953	0.944	0.91

TABLE V-15 (contd.)

0.8160	93.30	54.24	0.643091	0.993	1.090	1.089	0.04
0.8160	105.06	79.19	0.643091	1.024	1.591	1.604	-0.81
0.8160	120.09	112.66	0.643091	1.065	2.263	2.269	-0.24
0.8160	140.10	158.00	0.643091	1.119	3.174	3.165	0.29
0.7340	98.32	55.91	0.714935	1.006	1.123	1.126	-0.23
0.7340	105.19	67.53	0.714935	1.025	1.357	1.360	-0.23
0.7340	119.97	93.32	0.714935	1.065	1.875	1.869	0.34
0.7340	139.98	129.44	0.714935	1.119	2.601	2.567	1.29
0.6910	100.08	56.30	0.759425	1.011	1.131	1.138	-0.62
0.6910	119.99	86.90	0.759425	1.065	1.746	1.744	0.11
0.6910	129.94	102.30	0.759425	1.092	2.055	2.050	0.24
0.6910	139.98	118.52	0.759425	1.119	2.381	2.362	0.83
0.6240	104.80	60.28	0.840965	1.024	1.211	1.225	-1.11
0.6240	114.94	73.09	0.840965	1.051	1.468	1.484	-1.07
0.6240	129.80	93.18	0.840965	1.092	1.872	1.867	0.27
0.6240	139.94	105.76	0.840965	1.119	2.125	2.130	-0.24
0.5330	105.02	58.60	0.984545	1.024	1.177	1.184	-0.59
0.5330	120.21	74.08	0.984545	1.066	1.488	1.495	-0.46
0.5330	139.96	94.65	0.984545	1.119	1.902	1.900	0.11
0.4770	110.41	62.48	1.100131	1.039	1.255	1.255	-0.01
0.4770	120.20	71.15	1.100131	1.066	1.429	1.429	0.05
0.4770	139.96	88.54	1.100131	1.119	1.779	1.777	0.12
0.4290	104.92	56.76	1.223222	1.024	1.140	1.138	0.20
0.4290	119.98	68.46	1.223222	1.065	1.375	1.371	0.31
0.4290	139.98	83.78	1.223222	1.119	1.683	1.678	0.33
0.3770	99.90	52.14	1.391943	1.011	1.048	1.046	0.12
0.3770	109.92	58.92	1.391943	1.038	1.184	1.179	0.40
0.3770	125.04	68.90	1.391943	1.079	1.384	1.377	0.52
0.3770	140.00	78.74	1.391943	1.119	1.582	1.571	0.70
0.3460	99.66	51.34	1.516654	1.010	1.032	1.031	0.05

TABLE V-15 (contd.)

0.3460	110.07	57.67	1.516654	1.038	1.159	1.155	0.33
0.3460	125.02	66.59	1.516654	1.079	1.338	1.331	0.53
0.3460	139.81	75.17	1.516654	1.119	1.510	1.502	0.51
0.3100	99.62	50.29	1.692782	1.010	1.010	1.010	0.09
0.3100	110.00	55.83	1.692782	1.038	1.122	1.117	0.38
0.3100	124.86	63.51	1.692782	1.078	1.276	1.270	0.50
0.3100	139.96	71.12	1.692782	1.119	1.429	1.422	0.49
0.2780	95.08	46.76	1.887635	0.997	0.939	0.941	-0.15
0.2780	110.11	53.77	1.887635	1.038	1.080	1.077	0.27
0.2780	124.92	60.41	1.887635	1.078	1.214	1.209	0.35
0.2780	139.99	67.14	1.887635	1.119	1.349	1.342	0.54
0.2480	89.69	42.75	2.115977	0.983	0.859	0.868	-1.09
0.2480	104.90	48.77	2.115977	1.024	0.980	0.989	-0.92
0.2480	125.03	56.93	2.115977	1.079	1.144	1.145	-0.07
0.2480	140.03	62.56	2.115977	1.119	1.257	1.259	-0.12
0.2150	89.61	41.05	2.440755	0.983	0.825	0.829	-0.48
0.2150	104.97	46.36	2.440755	1.024	0.931	0.930	0.11
0.2150	115.07	49.49	2.440755	1.052	0.994	0.996	-0.18
0.2150	125.03	52.66	2.440755	1.079	1.058	1.060	-0.19
0.2150	139.82	57.28	2.440755	1.119	1.151	1.154	-0.24
0.1900	84.57	37.54	2.761907	0.969	0.754	0.759	-0.61
0.1900	94.82	40.55	2.761907	0.997	0.815	0.818	-0.35
0.1900	109.88	44.79	2.761907	1.038	0.900	0.902	-0.27
0.1900	125.00	48.92	2.761907	1.079	0.983	0.986	-0.27
0.1900	139.89	53.18	2.761907	1.119	1.069	1.066	0.21
0.1570	75.88	32.43	3.342436	0.945	0.652	0.654	-0.32
0.1570	94.71	36.85	3.342436	0.996	0.740	0.739	0.19
0.1570	110.17	40.30	3.342436	1.038	0.810	0.807	0.27
0.1570	124.92	43.50	3.342436	1.078	0.874	0.872	0.29
0.1570	140.09	46.38	3.342436	1.119	0.932	0.936	-0.47

TABLE V-15 (contd.)

0.1323	70.02	28.51	3.966458	0.930	0.573	0.575	-0.43
0.1323	85.15	31.39	3.966458	0.971	0.631	0.631	-0.09
0.1323	99.95	34.12	3.966458	1.011	0.685	0.685	0.08
0.1323	119.81	37.34	3.966458	1.064	0.750	0.755	-0.69
0.1323	140.22	41.13	3.966458	1.120	0.826	0.826	0.02
0.1068	62.07	23.99	4.913506	0.908	0.482	0.483	-0.26
0.1068	79.94	26.68	4.913506	0.956	0.536	0.534	0.31
0.1068	99.85	29.42	4.913506	1.010	0.591	0.590	0.19
0.1068	119.90	32.23	4.913506	1.065	0.648	0.645	0.43
0.1068	139.91	34.90	4.913506	1.119	0.701	0.698	0.43
0.0825	55.10	19.40	6.360757	0.889	0.390	0.392	-0.61
0.0825	69.89	20.98	6.360757	0.929	0.422	0.423	-0.41
0.0825	84.89	22.54	6.360757	0.970	0.453	0.454	-0.35
0.0825	110.13	25.06	6.360757	1.038	0.504	0.506	-0.40
0.0825	124.92	26.51	6.360757	1.078	0.533	0.535	-0.42

TABLE V-16

V-16. Comparison of Eqn. V-1 and Isothermal PVT Data for R-22 Reported by Zander (140)

Temp. t c	Pressure P bars	Compress. Factor Z	V/0.030525	T/664.5	P_{exp}/721.906	P_{calc}/721.906	%Dev.
30.00	10.75	0.828000	11.785273	0.821	0.216	0.217	-0.35
30.00	6.34	0.906900	21.883774	0.821	0.127	0.127	-0.01
30.00	5.93	0.913500	23.562679	0.821	0.119	0.119	0.00
30.00	3.33	0.953600	43.749172	0.821	0.067	0.067	0.07
30.00	3.11	0.956900	47.106568	0.821	0.062	0.062	0.07
50.00	17.97	0.753200	6.833082	0.875	0.361	0.363	-0.47
50.00	14.31	0.813200	9.267264	0.875	0.287	0.289	-0.46
50.00	10.42	0.873300	13.662027	0.875	0.209	0.209	-0.04
50.00	7.94	0.906200	18.597977	0.875	0.160	0.160	-0.00
50.00	5.59	0.935900	27.311513	0.875	0.112	0.112	0.03
50.00	4.18	0.952900	37.182627	0.875	0.084	0.084	0.05
50.00	2.89	0.967900	54.599709	0.875	0.058	0.058	0.04
70.00	28.50	0.651300	3.956292	0.930	0.573	0.576	-0.59
70.00	24.00	0.730600	5.270710	0.930	0.482	0.483	-0.24
70.00	17.84	0.815300	7.910128	0.930	0.359	0.359	-0.06
70.00	14.12	0.859500	10.537371	0.930	0.284	0.284	-0.00
70.00	9.91	0.905200	15.814748	0.930	0.199	0.199	0.03
70.00	7.63	0.928600	21.067764	0.930	0.153	0.153	0.06
70.00	5.22	0.952300	31.613223	0.930	0.105	0.105	0.06
70.00	3.96	0.964200	42.119367	0.930	0.080	0.080	0.06
100.00	58.69	0.225400	0.723031	1.011	1.179	1.172	0.64
100.00	55.29	0.235800	0.802904	1.011	1.111	1.113	-0.19
100.00	53.31	0.308000	1.087635	1.011	1.071	1.072	-0.06
100.00	52.94	0.339800	1.208362	1.011	1.064	1.063	0.10
100.00	51.11	0.431700	1.590255	1.011	1.027	1.027	0.02
100.00	50.88	0.442400	1.637070	1.011	1.022	1.021	0.14
100.00	49.63	0.479500	1.818790	1.011	0.997	0.996	0.12
100.00	45.09	0.573100	2.393049	1.011	0.906	0.905	0.05

TABLE V-16 (contd.)

100.00	44.52	0.582600	2.463865	1.011	0.894	0.894	0.05
100.00	42.37	0.616000	2.737186	1.011	0.851	0.851	0.07
100.00	36.27	0.694000	3.601920	1.011	0.729	0.729	0.01
100.00	35.63	0.701700	3.708124	1.011	0.716	0.716	0.03
100.00	33.26	0.727800	4.119140	1.011	0.668	0.668	0.04
100.00	27.29	0.785600	5.420554	1.011	0.548	0.549	-0.15
100.00	26.74	0.792500	5.580651	1.011	0.537	0.537	0.02
100.00	24.66	0.812000	6.199837	1.011	0.495	0.495	0.07
100.00	19.71	0.854300	8.158639	1.011	0.396	0.396	0.03
100.00	19.24	0.858200	8.398673	1.011	0.387	0.386	0.03
100.00	17.59	0.871700	9.331626	1.011	0.353	0.353	0.03
100.00	13.82	0.901500	12.281170	1.011	0.278	0.278	0.04
100.00	13.47	0.904200	12.640833	1.011	0.271	0.270	0.04
100.00	9.26	0.935800	19.023209	1.011	0.186	0.186	0.05
125.00	350.16	0.854500	0.490220	1.079	7.035	6.796	3.40
125.00	247.82	0.650400	0.527217	1.079	4.979	4.893	1.73
125.00	186.16	0.519300	0.560373	1.079	3.740	3.812	-1.92
125.00	97.46	0.357900	0.737732	1.079	1.958	1.961	-0.14
125.00	90.29	0.356600	0.793391	1.079	1.814	1.821	-0.41
125.00	86.07	0.361300	0.843240	1.079	1.729	1.740	-0.61
125.00	75.04	0.414800	1.110445	1.079	1.508	1.507	0.02
125.00	72.97	0.433800	1.194303	1.079	1.466	1.462	0.25
125.00	71.31	0.450600	1.269275	1.079	1.433	1.427	0.38
125.00	63.91	0.531700	1.671178	1.079	1.284	1.278	0.48
125.00	61.85	0.553400	1.797429	1.079	1.243	1.238	0.39
125.00	60.10	0.571500	1.910364	1.079	1.207	1.203	0.33
125.00	51.92	0.650200	2.515596	1.079	1.043	1.042	0.13
125.00	49.74	0.669800	2.705326	1.079	0.999	0.998	0.12
125.00	47.77	0.683800	2.875298	1.079	0.960	0.961	-0.17
125.00	39.80	0.750100	3.786007	1.079	0.800	0.800	-0.01

TABLE V-16 (contd.)

125.00	37.77	0.765600	4.071391	1.079	0.759	0.759	0.01
125.00	36.10	0.777600	4.326835	1.079	0.725	0.725	-0.02
125.00	29.14	0.826500	5.698079	1.079	0.585	0.586	-0.02
125.00	27.46	0.837700	6.128206	1.079	0.552	0.552	-0.02
125.00	26.11	0.846600	6.512786	1.079	0.525	0.525	-0.01
125.00	20.65	0.881600	8.575824	1.079	0.415	0.415	0.00
125.00	19.38	0.889600	9.219750	1.079	0.389	0.389	0.02
125.00	18.36	0.895900	9.804531	1.079	0.369	0.369	0.02
125.00	14.32	0.920300	12.909262	1.079	0.288	0.288	0.04
125.00	13.40	0.925800	13.876914	1.079	0.269	0.269	0.05
125.00	12.66	0.930100	14.756137	1.079	0.254	0.254	0.05
125.00	9.79	0.946700	19.429794	1.079	0.197	0.197	0.06
125.00	9.14	0.950400	20.883393	1.079	0.184	0.184	0.06
150.00	348.13	0.851200	0.522015	1.146	6.994	6.930	0.91
150.00	198.74	0.574000	0.616623	1.146	3.993	4.024	-0.78
150.00	128.51	0.472900	0.785643	1.146	2.582	2.566	0.63
150.00	109.58	0.476400	0.928183	1.146	2.202	2.200	0.06
150.00	93.25	0.516500	1.182574	1.146	1.873	1.868	0.31
150.00	84.88	0.555400	1.396991	1.146	1.705	1.696	0.54
150.00	73.90	0.616000	1.779604	1.146	1.485	1.479	0.41
150.00	66.83	0.658100	2.102359	1.146	1.343	1.339	0.31
150.00	57.03	0.715500	2.678688	1.146	1.146	1.144	0.15
150.00	50.70	0.751400	3.164081	1.146	1.019	1.018	0.07
150.00	42.25	0.797800	4.031345	1.146	0.849	0.849	0.02
150.00	37.01	0.825400	4.761826	1.146	0.744	0.744	-0.01
150.00	30.26	0.860100	6.067381	1.146	0.608	0.608	0.00
150.00	26.22	0.880300	7.168431	1.146	0.527	0.527	0.02
150.00	21.15	0.904900	9.132308	1.146	0.425	0.425	0.03
150.00	18.19	0.919000	10.787568	1.146	0.365	0.365	0.04
150.00	12.43	0.945600	16.235088	1.146	0.250	0.250	0.04

TABLE. V-16 (contd.)

150.00	8.42	0.963700	24.434134	1.146	0.169	0.169	0.05
150.00	5.66	0.975800	36.778997	1.146	0.114	0.114	0.04
200.00	346.80	0.877400	0.603971	1.282	6.968	6.940	0.40
200.00	257.87	0.741600	0.686541	1.282	5.181	5.101	1.53
200.00	170.27	0.648500	0.909221	1.282	3.421	3.395	0.75
200.00	149.34	0.646600	1.033611	1.282	3.000	2.990	0.35
200.00	117.85	0.675700	1.368743	1.282	2.368	2.362	0.25
200.00	106.74	0.695800	1.556162	1.282	2.145	2.141	0.17
200.00	86.26	0.744500	2.060501	1.282	1.733	1.733	0.00
200.00	76.12	0.766600	2.342602	1.282	1.570	1.571	-0.08
200.00	62.50	0.812000	3.101611	1.282	1.256	1.258	-0.19
200.00	56.25	0.830800	3.526163	1.282	1.130	1.132	-0.21
200.00	44.34	0.867300	4.669508	1.282	0.891	0.893	-0.19
200.00	39.64	0.881800	5.309812	1.282	0.797	0.798	-0.17
200.00	30.85	0.908600	7.029827	1.282	0.620	0.621	-0.14
200.00	27.45	0.918900	7.991701	1.282	0.551	0.552	-0.13
200.00	21.16	0.937800	10.582156	1.282	0.425	0.425	-0.10
200.00	18.75	0.945000	12.029804	1.282	0.377	0.377	-0.09
200.00	12.69	0.963000	18.111712	1.282	0.255	0.255	-0.06

TABLE V-17

V-17. Comparison of Eqn. V-1 and PVT Data for R-115
Reported by the University of Michigan (136)

Density d lbs/cuft	Temp. T R	Pressure P_{exp} psia	V/0.02681	T/635.56	$P_{exp}/456.0$	$P_{calc}/456.0$	%Dev.
1.1350	470.30	34.40	32.863009	0.740	0.075	0.075	0.38
1.1350	492.20	36.40	32.863009	0.774	0.080	0.079	0.67
1.1350	531.20	39.60	32.863009	0.836	0.087	0.087	0.28
1.1350	581.30	43.90	32.863009	0.915	0.096	0.096	0.40
1.1350	621.80	47.30	32.863009	0.978	0.104	0.103	0.39
1.1350	668.10	51.30	32.863009	1.051	0.112	0.112	0.66
1.1350	715.20	55.10	32.863009	1.125	0.121	0.120	0.45
1.1350	757.90	58.70	32.863009	1.192	0.129	0.128	0.58
1.2970	492.20	39.90	28.758300	0.774	0.087	0.090	-2.49
1.2970	535.50	44.50	28.758300	0.843	0.098	0.099	-1.49
1.2970	579.30	49.10	28.758300	0.911	0.108	0.108	-0.68
1.2970	620.00	52.70	28.758300	0.976	0.116	0.117	-1.25
1.2970	668.80	57.40	28.758300	1.052	0.126	0.127	-1.10
1.2970	717.00	62.10	28.758300	1.128	0.136	0.137	-0.81
1.2970	761.20	66.30	28.758300	1.198	0.145	0.146	-0.72
2.9650	534.50	94.00	12.579938	0.841	0.206	0.207	-0.27
2.9650	569.70	102.60	12.579938	0.896	0.225	0.226	-0.23
2.9650	611.00	112.80	12.579938	0.961	0.247	0.247	0.06
2.9650	661.90	124.70	12.579938	1.041	0.273	0.273	-0.01
2.9650	745.70	142.30	12.579938	1.173	0.312	0.316	-1.20
5.8850	571.60	179.40	6.338065	0.899	0.393	0.392	0.36
5.8850	614.10	201.70	6.338065	0.966	0.442	0.442	0.11
5.8850	651.30	220.70	6.338065	1.025	0.484	0.484	-0.07
5.8850	668.90	230.00	6.338065	1.052	0.504	0.504	0.05
5.8850	718.20	253.90	6.338065	1.130	0.557	0.559	-0.34
5.8850	764.40	276.50	6.338065	1.203	0.606	0.609	-0.41
7.0000	575.50	202.90	5.328502	0.906	0.445	0.447	-0.50
7.0000	593.70	214.60	5.328502	0.934	0.471	0.474	-0.67

TABLE V-17 (contd.)

7.0000	608.50	223.80	5.328502	0.957	0.491	0.495	-0.87
7.0000	646.10	247.80	5.328502	1.017	0.543	0.548	-0.89
7.0000	670.20	263.20	5.328502	1.055	0.577	0.582	-0.78
7.0000	701.30	282.50	5.328502	1.103	0.620	0.624	-0.76
7.0000	730.20	299.90	5.328502	1.149	0.658	0.663	-0.83
7.0000	754.10	314.40	5.328502	1.187	0.689	0.695	-0.79
16.6750	619.80	373.00	2.236852	0.975	0.818	0.826	-0.93
16.6750	646.20	430.10	2.236852	1.017	0.943	0.938	0.58
16.6750	718.00	564.30	2.236852	1.130	1.237	1.232	0.45
16.6750	802.70	714.20	2.236852	1.263	1.566	1.564	0.15
16.6750	886.90	866.30	2.236852	1.395	1.900	1.883	0.90
23.0420	638.90	455.60	1.618762	1.005	0.999	0.997	0.19
23.0420	645.60	475.60	1.618762	1.016	1.043	1.040	0.26
23.0420	696.90	623.60	1.618762	1.097	1.368	1.364	0.23
23.0420	766.90	822.10	1.618762	1.207	1.803	1.793	0.53
23.0420	786.60	876.40	1.618762	1.238	1.922	1.912	0.53
23.0420	837.60	1016.90	1.618762	1.318	2.230	2.215	0.68
27.7210	639.10	465.90	1.345533	1.006	1.022	1.024	-0.27
27.7210	674.40	595.80	1.345533	1.061	1.307	1.311	-0.32
27.7210	743.00	843.30	1.345533	1.169	1.849	1.856	-0.35
27.7210	813.90	1099.70	1.345533	1.281	2.412	2.407	0.18
27.7210	862.80	1274.10	1.345533	1.358	2.794	2.782	0.42
37.5040	642.00	487.70	0.994548	1.010	1.070	1.077	-0.71
37.5040	663.50	601.10	0.994548	1.044	1.318	1.334	-1.22
37.5040	688.00	735.40	0.994548	1.083	1.613	1.627	-0.91
37.5040	737.40	1008.30	0.994548	1.160	2.211	2.219	-0.34
37.5040	790.70	1307.00	0.994548	1.244	2.866	2.857	0.33
42.0100	633.50	439.00	0.887872	0.997	0.963	0.972	-0.99
42.0100	641.70	487.00	0.887872	1.010	1.068	1.085	-1.62
42.0100	663.70	626.00	0.887872	1.044	1.373	1.390	-1.24

TABLE V-17 (contd.)

42.0100	688.60	790.00	0.887872	1.083	1.732	1.736	-0.23
42.0100	713.10	948.00	0.887872	1.122	2.079	2.079	-0.01
42.0100	747.80	1180.00	0.887872	1.177	2.588	2.567	0.80

TABLE V-18

V-18. Comparison of Eqn. V-1 and PVT Data for R-115 Reported by Mears et al. (98)

Volume V cuft/lb	Temp. T R	Pressure P_{exp} psia	V/0.02681	T/635.56	P_{exp}/456.0	P_{calc}/456.0	%Dev.
0.018107	634.842	502.309	0.675392	0.999	1.102	1.100	0.16
0.018112	644.022	598.274	0.675571	1.013	1.312	1.314	-0.15
0.018117	653.112	694.533	0.675751	1.028	1.523	1.527	-0.25
0.018122	661.896	790.057	0.675930	1.041	1.733	1.733	-0.04
0.018126	671.670	894.692	0.676109	1.057	1.962	1.964	-0.09
0.018131	680.526	993.156	0.676288	1.071	2.178	2.173	0.22
0.026568	635.508	459.103	0.990981	1.000	1.007	0.999	0.73
0.026575	644.616	507.453	0.991220	1.014	1.113	1.109	0.36
0.026583	653.688	555.656	0.991519	1.029	1.219	1.218	0.07
0.026587	661.014	595.482	0.991698	1.040	1.306	1.306	0.02
0.026597	671.688	653.678	0.992057	1.057	1.434	1.434	-0.01
0.026603	680.688	702.616	0.992296	1.071	1.541	1.541	-0.04
0.026611	689.688	751.259	0.992595	1.085	1.647	1.649	-0.11
0.026618	698.688	800.491	0.992834	1.099	1.755	1.757	-0.09
0.026626	707.634	849.282	0.993132	1.113	1.862	1.864	-0.08
0.026640	725.706	949.068	0.993670	1.142	2.081	2.080	0.06
0.027773	635.598	459.544	1.035912	1.000	1.008	1.000	0.73
0.027779	644.634	504.367	1.036151	1.014	1.106	1.103	0.26
0.027787	653.688	551.394	1.036450	1.029	1.209	1.206	0.27
0.027795	662.670	597.098	1.036748	1.043	1.309	1.308	0.13
0.027803	671.706	643.538	1.037047	1.057	1.411	1.410	0.09
0.027818	689.634	735.241	1.037585	1.085	1.612	1.613	-0.01
0.027824	707.598	827.826	1.037824	1.113	1.815	1.815	0.00
0.027837	725.598	920.117	1.038302	1.142	2.018	2.018	-0.01
0.027861	743.688	1013.583	1.039198	1.170	2.223	2.220	0.10
0.030486	635.688	456.017	1.137125	1.000	1.000	1.001	-0.11
0.030496	644.742	498.047	1.137484	1.014	1.092	1.093	-0.05
0.030506	653.688	539.196	1.137842	1.029	1.182	1.183	-0.04

TABLE V-18 (contd.)

0.030522	671.688	621.200	1.138440	1.057	1.362	1.364	-0.11
0.030538	689.706	703.057	1.139037	1.085	1.542	1.544	-0.13
0.030552	707.688	783.444	1.139575	1.113	1.718	1.723	-0.26
0.030570	725.688	863.684	1.140232	1.142	1.894	1.901	-0.35
0.030586	743.778	943.777	1.140829	1.170	2.070	2.079	-0.45
0.030602	756.378	1001.091	1.141427	1.190	2.195	2.202	-0.32
0.037664	635.688	451.608	1.404856	1.000	0.990	0.994	-0.32
0.037687	653.706	517.593	1.405693	1.029	1.135	1.132	0.24
0.037706	671.688	580.345	1.406410	1.057	1.273	1.270	0.25
0.037727	689.724	641.333	1.407186	1.085	1.406	1.406	0.05
0.037744	707.706	702.175	1.407844	1.114	1.540	1.540	-0.03
0.037765	725.742	762.428	1.408620	1.142	1.672	1.674	-0.13
0.037786	743.742	821.947	1.409397	1.170	1.803	1.807	-0.23
0.037805	761.688	880.731	1.410114	1.198	1.931	1.938	-0.33
0.049262	630.054	418.395	1.837432	0.991	0.918	0.920	-0.27
0.049270	635.670	433.238	1.837731	1.000	0.950	0.951	-0.07
0.049298	653.940	480.265	1.838806	1.029	1.053	1.050	0.31
0.049326	671.688	523.471	1.839822	1.057	1.148	1.145	0.26
0.049351	689.580	567.413	1.840778	1.085	1.244	1.239	0.39
0.049375	707.616	609.002	1.841674	1.113	1.336	1.334	0.14
0.049403	725.580	651.180	1.842690	1.142	1.428	1.426	0.11
0.049428	743.706	693.063	1.843646	1.170	1.520	1.519	0.06
0.049455	761.616	733.183	1.844662	1.198	1.608	1.609	-0.10
0.049481	779.724	774.626	1.845618	1.227	1.699	1.700	-0.09
0.049495	788.778	794.613	1.846155	1.241	1.743	1.745	-0.15
0.049508	797.778	814.011	1.846633	1.255	1.785	1.790	-0.26
0.070414	617.832	351.528	2.626405	0.972	0.771	0.772	-0.15
0.070452	635.688	380.322	2.627839	1.000	0.834	0.834	0.05
0.070494	653.688	409.284	2.629393	1.029	0.898	0.895	0.31
0.070532	671.868	437.941	2.630827	1.057	0.960	0.956	0.50

TABLE V-18 (contd.)

0.070569	689.796	463.218	2.632201	1.085	1.016	1.015	0.11
0.070603	707.544	490.112	2.633455	1.113	1.075	1.072	0.22
0.070643	725.616	515.977	2.634949	1.142	1.132	1.131	0.08
0.070680	743.742	541.695	2.636323	1.170	1.188	1.188	-0.02
0.070718	761.688	568.000	2.637757	1.198	1.246	1.245	0.08
0.070755	779.706	593.571	2.639132	1.227	1.302	1.301	0.08
0.070794	797.706	618.995	2.640566	1.255	1.357	1.356	0.10
0.107293	600.012	266.438	4.001985	0.944	0.584	0.582	0.47
0.107397	635.562	300.827	4.005868	1.000	0.660	0.653	0.95
0.107530	671.634	333.599	4.010828	1.057	0.732	0.724	1.02
0.107639	707.598	365.343	4.014890	1.113	0.801	0.793	1.03
0.107698	725.670	380.332	4.017101	1.142	0.834	0.827	0.86
0.107698	725.580	380.185	4.017101	1.142	0.834	0.827	0.84
0.107755	747.162	397.821	4.019192	1.176	0.872	0.867	0.64
0.107871	779.688	426.478	4.023554	1.227	0.935	0.926	0.96
0.107964	808.668	450.432	4.027019	1.272	0.988	0.979	0.93
0.107330	587.610	252.477	4.003359	0.925	0.554	0.556	-0.37
0.107343	591.372	257.474	4.003837	0.930	0.565	0.564	0.20
0.107399	609.192	274.374	4.005928	0.959	0.602	0.600	0.27
0.107461	626.308	292.156	4.008258	0.989	0.641	0.639	0.33
0.107577	665.172	325.222	4.012560	1.047	0.713	0.711	0.27
0.107706	705.006	360.640	4.017400	1.109	0.791	0.788	0.41
0.107815	738.612	389.150	4.021463	1.162	0.853	0.850	0.34
0.107936	775.278	420.159	4.025944	1.220	0.921	0.918	0.40
0.160676	564.102	181.643	5.993149	0.888	0.398	0.398	0.04
0.160849	597.906	202.364	5.999601	0.941	0.444	0.441	0.71
0.161006	634.662	223.085	6.005457	0.999	0.489	0.486	0.74
0.161205	673.362	243.660	6.012866	1.059	0.534	0.532	0.50
0.161368	709.308	262.764	6.018960	1.116	0.576	0.574	0.46
0.161543	744.948	282.310	6.025472	1.172	0.619	0.614	0.78

TABLE V-18 (contd.)

0.161716	779.544	300.239	6.031925	1.227	0.658	0.653	0.79
0.161855	806.094	313.760	6.037123	1.268	0.688	0.683	0.79

TABLE V-19

V-19. Comparison of Eqn. V-1 and PVT Data of R-502

V cuft/lb	T R	P_{exp} psia	$\underline{V}$/0.028622	T/638.23	P_{exp}/593.79	P_{calc}/593.79	% Dev.
0.582420	541.140	81.950	20.348683	0.848	0.138	0.137	0.71
0.466240	541.130	99.620	16.289567	0.848	0.168	0.167	0.39
0.404380	541.140	116.940	14.128293	0.848	0.197	0.189	3.96
0.307140	541.140	141.290	10.730906	0.848	0.238	0.238	-0.04
0.248410	541.140	166.230	8.678988	0.848	0.280	0.281	-0.47
0.216550	541.130	178.800	7.565858	0.848	0.301	0.311	-3.39
0.577660	639.490	100.030	20.182377	1.002	0.168	0.169	-0.06
0.461020	639.490	123.530	16.107190	1.002	0.208	0.208	0.06
0.358770	639.640	154.190	12.534763	1.002	0.260	0.261	-0.65
0.345300	639.500	160.530	12.064146	1.002	0.270	0.270	-0.02
0.287570	639.620	168.540	10.047167	1.002	0.318	0.318	-0.14
0.279680	639.500	193.430	9.771504	1.002	0.326	0.326	0.02
0.225160	639.530	232.430	7.866676	1.002	0.391	0.392	-0.13
0.172130	639.610	288.490	6.013905	1.002	0.486	0.487	-0.33
0.139340	639.610	338.240	4.868283	1.002	0.570	0.572	-0.43
0.111480	639.630	393.490	3.894906	1.002	0.663	0.668	-0.79
0.054600	639.590	555.360	1.907624	1.002	0.935	0.947	-1.29
0.049090	639.600	569.260	1.715114	1.002	0.959	0.973	-1.49
0.045340	639.600	576.260	1.584096	1.002	0.970	0.988	-1.77
0.042200	639.600	581.760	1.474390	1.002	0.980	0.998	-1.84
0.037760	639.620	586.260	1.319265	1.002	0.987	1.008	-2.09
0.037560	639.580	586.770	1.312277	1.002	0.988	1.008	-2.00
0.023180	639.570	590.280	0.809867	1.002	0.994	1.026	-3.25
0.022820	639.540	594.270	0.797289	1.002	1.001	1.029	-2.80
0.021370	639.600	603.260	0.746628	1.002	1.016	1.054	-3.73
0.020370	639.560	624.270	0.711690	1.002	1.051	1.090	-3.64
0.019880	639.570	634.260	0.694571	1.002	1.068	1.118	-4.62
0.018300	639.600	729.610	0.639368	1.002	1.229	1.288	-4.80

TABLE V-19 (contd.)

0.017680	639.530	806.470	0.617707	1.002	1.358	1.409	-3.77
0.016980	639.560	930.270	0.593250	1.002	1.567	1.618	-3.25
0.016430	639.550	1068.270	0.574034	1.002	1.799	1.853	-2.97
0.015960	639.560	1224.270	0.557613	1.002	2.062	2.123	-2.98
0.015510	639.540	1418.290	0.541891	1.002	2.389	2.459	-2.94
0.015180	639.570	1602.290	0.530361	1.002	2.698	2.766	-2.51
0.014830	639.580	1837.790	0.518133	1.002	3.095	3.158	-2.05
0.014660	639.580	1975.290	0.512193	1.002	3.327	3.377	-1.53
0.037610	664.060	707.740	1.314024	1.040	1.192	1.212	-1.65
0.028910	664.040	751.740	1.010062	1.040	1.266	1.298	-2.50
0.025060	664.050	782.540	0.875550	1.040	1.318	1.356	-2.88
0.022280	664.040	834.040	0.778422	1.040	1.405	1.436	-2.23
0.020380	664.030	909.740	0.712040	1.040	1.532	1.577	-2.96
0.018730	664.030	1051.640	0.654392	1.040	1.771	1.854	-4.68
0.017050	664.040	1366.820	0.595696	1.040	2.302	2.423	-5.27
0.016240	664.060	1650.220	0.567396	1.040	2.779	2.857	-2.79
0.015630	664.050	1962.320	0.546083	1.040	3.305	3.268	1.10
0.108940	666.150	433.400	3.806163	1.044	0.730	0.734	-0.57
0.086400	666.130	503.160	3.018657	1.044	0.847	0.855	-0.86
0.063970	666.140	593.460	2.234994	1.044	0.999	1.009	-0.98
0.043500	666.150	689.260	1.519810	1.044	1.161	1.177	-1.42
0.033780	666.140	736.960	1.180211	1.044	1.241	1.265	-1.95
0.107400	708.990	488.710	3.752358	1.111	0.823	0.831	-1.00
0.087960	708.960	563.510	3.073161	1.111	0.949	0.961	-1.27
0.071050	708.970	649.010	2.482356	1.111	1.093	1.109	-1.46
0.055680	708.960	752.010	1.945357	1.111	1.266	1.285	-1.45
0.040880	709.040	882.510	1.428272	1.111	1.486	1.515	-1.95
0.033170	708.950	977.000	1.158899	1.111	1.645	1.685	-2.41
0.038760	712.500	924.600	1.354203	1.116	1.557	1.584	-1.71
0.032100	712.540	1016.600	1.121515	1.116	1.712	1.750	-2.24

TABLE V-19 (contd.)

0.026050	712.560	1151.600	0.910139	1.116	1.939	1.978	-1.98
0.022850	712.570	1289.300	0.798337	1.116	2.171	2.185	-0.61
0.020830	712.580	1445.900	0.727762	1.116	2.435	2.465	-1.25
0.019480	712.570	1613.300	0.680595	1.116	2.717	2.827	-4.05
0.018680	712.590	1759.000	0.652645	1.117	2.962	3.148	-6.27
0.017870	712.610	1956.200	0.624345	1.117	3.294	3.569	-8.34

TABLE V-20

V-20. Comparison of Eqn. V-8 and Vapor Pressure Values for R-22 Reported by Booth and Swinehart (17)

t F	P psia	P_{eq} psia	Percent Deviation
72.68	138.000	141.788	-2.75
88.52	175.900	179.209	-1.88
88.70	177.400	179.672	-1.28
104.18	218.500	222.900	-2.01
105.98	225.000	228.381	-1.50
122.54	286.000	283.578	0.85
140.54	353.900	354.149	-0.07
148.46	376.700	389.030	-3.27
159.06	435.600	439.700	-0.94
160.70	450.000	447.968	0.45
177.98	531.000	542.638	-2.19
177.98	528.600	542.638	-2.66
185.72	576.500	589.899	-2.32
195.80	663.200	656.556	1.00
202.10	671.500	701.495	-4.47
202.64	689.800	705.476	-2.27
203.54	697.200	712.158	-2.15
204.80	706.600	721.615	-2.13
205.34	707.900	725.705	-2.52

TABLE V-21

V-21. Comparison of Eqn. V-8 and Vapor Pressure Values for R-22 Reported by Benning and McHarness (12)

t F	P psia	P_{eq} psia	Percent Deviation
-78.27	5.100	5.053	0.91
-41.19	14.800	14.752	0.33
23.00	61.700	61.088	0.99
77.27	152.400	151.972	0.28
168.62	488.900	489.598	-0.14
198.68	674.800	676.765	-0.29

TABLE V-22

V-22. Comparison of Eqn. V-8 and Vapor Pressure Values for R-22 Reported by Du Pont (46)

t F	P psia	P_{eq} psia	Percent Deviation
-155.00	0.209	0.209	0.11
-135.00	0.566	0.565	0.09
115.00	1.345	1.344	0.08
-95.00	2.873	2.871	0.07
-75.00	5.611	5.607	0.06
-55.00	10.166	10.160	0.06
-35.00	17.290	17.281	0.05
-15.00	27.865	27.852	0.05
10.00	47.464	47.445	0.04
30.00	69.591	69.566	0.04
50.00	98.727	98.694	0.03
70.00	136.120	136.081	0.03
90.00	183.090	183.042	0.03
110.00	241.040	240.979	0.03
130.00	311.500	311.419	0.03
150.00	396.190	396.102	0.02
170.00	497.260	497.149	0.02
190.00	617.590	617.460	0.02
204.81	721.910	721.691	0.03

TABLE V-23

V-23. Comparison of Eqn. V-8 and Vapor Pressure Values for R-22 Reported by Downing (42)

t F	P psia	P_{eq} psia	Percent Deviation
-50.00	11.700	11.667	0.28
-40.00	15.300	15.214	0.56
-30.00	19.700	19.563	0.70
-20.00	25.000	24.833	0.67
-10.00	31.300	31.148	0.48
0.0	38.800	38.640	0.41
10.00	47.600	47.445	0.32
20.00	58.000	57.705	0.51
30.00	69.900	69.566	0.48
40.00	83.700	83.177	0.62
50.00	99.400	98.694	0.71
60.00	117.200	116.275	0.79
70.00	137.200	136.081	0.82
80.00	159.700	158.279	0.89

TABLE V-24

V-24. Comparison of Eqn. V-8 and Vapor Pressure Values for R-22 Reported by Zander (140)

t F	P psia	P_{eq} psia	Percent Deviation
-93.69	3.000	3.007	-0.25
-79.46	4.880	4.863	0.34
-79.39	4.890	4.874	0.32
-58.51	9.230	9.198	0.34
-41.43	14.720	14.660	0.41
-38.12	16.020	15.967	0.33
-4.07	35.520	35.440	0.22
13.76	51.200	51.125	0.15
32.01	72.240	72.156	0.12
68.00	132.000	131.934	0.05
76.98	151.500	151.313	0.12
85.50	171.700	171.570	0.08
104.16	223.000	222.840	0.07
104.25	223.300	223.111	0.08
122.72	284.500	284.228	0.10
140.20	353.100	352.706	0.11
149.31	393.300	392.922	0.10
158.20	435.900	435.412	0.11
167.23	482.900	482.083	0.17
185.00	586.600	585.365	0.21
194.25	646.400	645.903	0.08
199.26	677.700	680.902	-0.47
203.18	709.200	709.478	-0.04

TABLE V-25

V-25. Comparison of Eqn. V-8 and Vapor Pressure Values for R-115 Reported by the University of Michigan (136)

t F	P psia	P_{eq} psia	Percent Deviation
-135.54	0.551	0.546	0.87
-113.71	1.380	1.377	0.26
-46.80	11.682	11.766	-0.72
-3.80	31.645	32.154	-1.61
10.65	42.335	43.051	-1.69
62.91	106.020	106.896	-0.83
87.33	152.370	153.548	-0.77
113.27	216.150	218.030	-0.87
140.56	302.860	305.575	-0.90
168.82	419.860	421.977	-0.50
172.48	436.090	439.312	-0.74
175.89	453.000	456.000	-0.66

TABLE V-26

V-26. Comparison of Eqn. V-8 and Vapor Pressure Values for R-115 Reported by Mears et al. (98)

t F	P psia	P_{eq} psia	Percent Deviation
-89.07	3.398	3.366	0.93
-59.46	8.460	8.349	1.31
-39.50	14.370	14.187	1.27
-21.59	21.750	21.793	-0.20
-3.59	32.330	32.295	0.11
14.02	46.590	45.953	1.37
30.76	63.050	62.624	0.68
31.85	64.810	63.848	1.48
49.68	87.150	86.533	0.71
67.21	115.900	114.222	1.45
85.10	148.100	148.758	-0.44
85.93	150.500	150.528	-0.02
94.96	170.800	170.803	-0.00
102.67	188.600	189.654	-0.56
103.87	192.500	192.721	-0.11
109.25	205.700	206.923	-0.59
112.94	217.500	217.102	0.18
121.75	243.400	242.903	0.20
128.05	260.600	262.704	-0.81
130.98	273.200	272.312	0.32
134.63	283.300	284.647	-0.48
139.98	304.100	303.478	0.20
145.38	321.800	323.424	-0.50
147.86	332.100	332.911	-0.24
149.02	338.300	337.421	0.26
156.92	368.400	369.393	-0.27
158.04	372.400	374.109	-0.46
162.32	391.100	392.567	-0.38

TABLE V-27

V-27. Comparison of Eqn. V-8 and Vapor Pressure Values for R-115 Reported by Aston et al. (4)

t F	P psia	P_{eq} psia	Percent Deviation
-139.58	0.453	0.453	0.20
-130.59	0.685	0.682	0.45
-116.38	1.247	1.238	0.66
-85.17	3.872	3.830	1.09
-68.85	6.434	6.367	1.03
-54.07	9.786	9.691	0.97
-39.74	14.219	14.102	0.82
-38.62	14.623	14.504	0.82

TABLE V-28

V-28. Comparison of Eqn. V-8 and Vapor Pressure Values for R-115 Reported by Downing (42)

t F	P psia	P_{eq} psia	Percent Deviation
-50.00	10.700	10.813	-1.06
-40.00	13.900	14.010	-0.79
-30.00	17.700	17.905	-1.16
-20.00	22.400	22.596	-0.88
-10.00	27.900	28.188	-1.03
0.0	34.400	34.787	-1.13
10.00	42.000	42.507	-1.21
20.00	50.800	51.465	-1.31
30.00	61.000	61.781	-1.28
40.00	72.600	73.579	-1.35
50.00	85.900	86.988	-1.27
60.00	100.800	102.140	-1.33
70.00	117.700	119.170	-1.25
80.00	136.600	138.219	-1.19

TABLE V-29

V-29. Comparison of Eqn. V-8 and Vapor Pressure Values for R-502 of This Work

t F	P psia	P_{eq} psia	Percent Deviation
-151.12	0.400	0.381	4.78
-129.88	1.097	1.015	7.54
-118.68	1.712	1.609	6.01
-117.14	1.719	1.709	0.57
-109.65	2.296	2.277	0.86
-109.60	2.307	2.281	1.15
-109.51	2.329	2.288	1.74
-109.19	2.445	2.316	5.28
-108.83	2.398	2.347	2.14
-103.45	2.958	2.856	3.44
-98.03	3.481	3.457	0.69
-97.37	3.523	3.537	-0.40
-88.89	4.851	4.702	3.06
-88.49	4.911	4.764	2.99
-78.45	6.452	6.546	-1.46
-76.95	6.890	6.854	0.53
-71.57	8.322	8.052	3.25
-67.71	8.916	9.011	-1.06
-65.82	9.338	9.512	-1.87
-56.96	11.860	12.169	-2.60
-55.19	12.304	12.764	-3.73
-54.85	12.901	12.880	0.16
-49.71	14.265	14.753	-3.42
-43.02	16.725	17.503	-4.65
98.46	224.380	230.204	-2.60
98.48	226.530	230.265	-1.65
98.58	225.350	230.574	-2.32
100.52	232.050	236.619	-1.97

TABLE V-29 (contd.)

100.54	233.060	236.681	-1.55
102.71	240.780	243.583	-1.16
110.85	266.630	270.818	-1.57
120.98	302.770	307.830	-1.67
130.04	335.080	344.070	-2.68
130.05	336.620	344.111	-2.23
130.23	339.630	345.281	-1.66
139.51	379.100	385.369	-1.65
147.26	414.900	421.976	-1.71
149.22	424.200	431.660	-1.76
150.38	433.100	437.476	-1.01
150.42	430.300	437.677	-1.71
152.41	436.860	447.807	-2.51
152.50	435.550	448.269	-2.92
163.27	497.110	506.598	-1.91
164.66	499.940	514.580	-2.93
169.55	527.450	543.569	-3.06
179.65	588.800	608.500	-3.35
179.74	589.340	609.114	-3.36
179.75	589.340	609.183	-3.37

TABLE V-30

V-30. Comparison of Eqn. V-8 and Vapor Pressure Values for R-502 Reported by Badylkes (5,6,7)

t F	P psia	P_{eq} psia	Percent Deviation
-112.00	2.121	2.084	1.74
-103.00	2.942	2.902	1.35
-94.00	4.014	3.968	1.15
-85.00	5.382	5.332	0.92
-76.00	7.106	7.054	0.73
-67.00	9.250	9.197	0.58
-58.00	11.880	11.829	0.43
-49.00	15.070	15.027	0.28
-40.00	18.900	18.869	0.16
-31.00	23.450	23.440	0.04
-22.00	28.810	28.828	-0.06
-13.00	35.070	35.126	-0.16
-4.00	42.320	42.429	-0.26
5.00	50.660	50.837	-0.35
14.00	60.180	60.452	-0.45
23.00	70.990	71.381	-0.55
32.00	83.190	83.729	-0.65
41.00	96.880	97.610	-0.75
50.00	112.190	113.137	-0.84
59.00	129.210	130.427	-0.94
68.00	148.100	149.602	-1.01
77.00	168.900	170.787	-1.12
86.00	191.800	194.114	-1.21
95.00	217.000	219.722	-1.25
104.00	244.500	247.756	-1.33

TABLE V-31

V-31. Comparison of Eqn. V-8 and Vapor Pressure Values for R-502 Reported by Loffler (86)

t F	P psia	P_{eq} psia	Percent Deviation
-112.00	2.146	2.084	2.89
-103.00	3.000	2.902	3.25
-94.00	4.100	3.968	3.22
-85.00	5.526	5.332	3.50
-76.00	7.320	7.054	3.63
-67.00	9.550	9.197	3.70
-58.00	12.290	11.829	3.75
-49.00	15.580	15.027	3.55
-40.00	19.550	18.869	3.48
-31.00	24.400	23.440	3.93
-22.00	29.980	28.828	3.84
-13.00	36.450	35.126	3.63
-4.00	43.940	42.429	3.44
5.00	52.610	50.837	3.37
14.00	62.460	60.452	3.21
23.00	73.770	71.381	3.24
32.00	86.410	83.729	3.10
41.00	100.500	97.610	2.88
50.00	116.200	113.137	2.64
59.00	133.700	130.427	2.45
68.00	153.100	149.602	2.28
77.00	174.600	170.787	2.18
86.00	198.000	194.114	1.96
95.00	223.700	219.722	1.78
104.00	251.900	247.756	1.64
113.00	282.500	278.377	1.46
122.00	315.800	311.758	1.28
131.00	352.100	348.093	1.14

TABLE V-31 (contd.)

140.00	391.700	387.606	1.05
149.00	434.400	430.564	0.88
158.00	480.900	477.302	0.75
167.00	531.100	528.272	0.53
176.00	585.800	584.166	0.28
180.90	617.300	617.092	0.03

TABLE V-32

V-32. Comparison of Eqn. V-8 and Vapor Pressure Values for R-502 Reported by Downing (42)

t F	P psia	P_{eq} psia	Percent Deviation
-20.00	29.800	30.146	-1.16
-10.00	37.600	37.444	0.42
-10.00	36.900	37.444	-1.47
0.0	46.000	46.023	-0.05
10.00	56.000	56.023	-0.04
20.00	67.500	67.585	-0.13
30.00	80.100	80.857	-0.94
40.00	95.200	95.989	-0.83
40.00	95.700	95.989	-0.30
50.00	111.600	113.137	-1.38
60.00	130.800	132.462	-1.27
70.00	150.700	154.131	-2.28
80.00	176.100	178.318	-1.26
90.00	201.100	205.205	-2.04
100.00	230.800	234.987	-1.81
110.00	260.500	267.872	-2.83
110.00	265.000	267.872	-1.08
130.00	332.700	343.903	-3.37
150.00	419.700	435.564	-3.78

TABLE V-33

V-33. Comparison of Eqn. V-8 and Vapor Pressure Values for R-502 Reported by Du Pont (47)

t F	P psia	P_{eq} psia	Percent Deviation
-100.00	3.230	3.228	0.07
-80.00	6.280	6.241	0.62
-60.00	11.280	11.198	0.72
-40.00	18.970	18.869	0.53
-20.00	30.220	30.146	0.25
0.0	45.940	46.023	-0.18
20.00	67.140	67.585	-0.66
40.00	94.900	95.989	-1.15
60.00	130.300	132.462	-1.66
80.00	174.600	178.318	-2.13
100.00	229.100	234.987	-2.57
120.00	295.000	304.092	-3.08
140.00	373.800	387.606	-3.69
160.00	467.300	488.244	-4.48

TABLE V-34

V-34. Comparison of Eqn. V-19 and Saturated Liquid Density Data for R-22 Reported by Benning and McHarness (14)

t F	d lbs/cu.ft.	d_{eq} lbs/cu.ft.	Percent Deviation
-92.20	93.074	93.050	0.03
-28.61	86.819	86.850	-0.04
24.57	81.094	81.075	0.02
79.14	74.259	74.237	0.03
122.41	67.672	67.648	0.04
152.01	61.929	61.973	-0.07
175.59	55.986	55.966	0.04
189.16	51.023	51.062	-0.08

TABLE V-35

V-35. Comparison of Eqn. V-19 and Saturated Liquid Density Values for R-22 Reported by Du Pont (46)

t F	d lbs/cu.ft.	d_{eq} lbs/cu.ft.	Percent Deviation
-155.00	98.669	98.671	-0.00
-130.00	96.480	96.482	-0.00
-110.00	94.684	94.686	-0.00
-90.00	92.843	92.845	-0.00
-70.00	90.952	90.954	-0.00
-50.00	89.004	89.006	-0.00
-30.00	86.991	86.993	-0.00
-10.00	84.901	84.904	-0.00
10.00	82.724	82.726	-0.00
30.00	80.441	80.444	-0.00
50.00	78.033	78.035	-0.00
70.00	75.469	75.471	-0.00
90.00	72.708	72.711	-0.00
110.00	69.689	69.692	-0.00
130.00	66.312	66.316	-0.01
150.00	62.402	62.406	-0.01
170.00	57.581	57.587	-0.01
190.00	50.677	50.686	-0.02
204.81	32.760	34.497	-5.30

TABLE V-36

V-36. Comparison of Eqn. V-19 and Saturated Liquid Density Values for R-22 Reported by Zander (140)

t F	d lbs/cu.ft.	d_{eq} lbs/cu.ft.	Percent Deviation
32.00	79.987	80.209	-0.28
44.83	78.445	78.671	-0.29
54.66	77.234	77.453	-0.28
61.30	76.391	76.608	-0.28
62.85	76.198	76.408	-0.28
65.79	75.811	76.026	-0.28
67.06	75.649	75.860	-0.28
68.13	75.517	75.719	-0.27
76.59	74.388	74.586	-0.27
84.54	73.301	73.487	-0.25
86.02	73.077	73.278	-0.28
88.47	72.752	72.930	-0.24
95.40	71.747	71.924	-0.25
104.47	70.380	70.557	-0.25
112.19	69.169	69.342	-0.25
113.20	69.019	69.179	-0.23
121.03	67.758	67.883	-0.18
123.75	67.265	67.418	-0.23
131.50	65.916	66.044	-0.19
137.21	64.899	64.981	-0.13
142.41	63.837	63.970	-0.21
152.51	61.771	61.863	-0.15
157.17	60.729	60.815	-0.14
161.55	59.749	59.775	-0.04
171.12	57.189	57.275	-0.15
173.88	56.415	56.479	-0.11
176.90	55.510	55.561	-0.09
187.63	51.652	51.717	-0.13

TABLE V-36 (contd.)

188.83	51.165	51.206	-0.08
191.55	49.935	49.958	0.05
196.61	47.207	47.144	0.13

TABLE V-37

V-37. Comparison of Eqn. V-19 and Saturated Liquid Density Values for R-115 Reported by the University of Michigan (136)

t F	d lbs/cu.ft.	d_{eq} lbs/cu.ft.	Percent Deviation
172.83	49.189	49.337	-0.30
153.50	61.656	61.950	-0.48
118.09	72.200	72.369	-0.23
101.97	75.634	75.818	-0.24
68.32	82.333	81.883	0.55
13.62	90.130	89.962	0.19
10.71	90.455	90.353	0.11
-36.04	96.423	96.279	0.15
-39.15	96.860	96.654	0.21
-143.21	108.247	108.268	-0.02

TABLE V-38

V-38. Comparison of Eqn. V-19 and Saturated Liquid Density Values for R-115 Reported by Mears et al. (98)

t F	d lbs/cu.ft.	d_{eq} lbs/cu.ft.	Percent Deviation
-104.33	103.967	104.100	-0.13
-3.71	92.156	92.248	-0.10
16.43	89.528	89.582	-0.06
44.90	85.433	85.538	-0.12
62.53	82.729	82.821	-0.11
76.98	80.170	80.431	-0.33
85.94	78.559	78.858	-0.38
94.96	77.005	77.187	-0.24
103.28	75.375	75.555	-0.24
112.98	73.315	73.515	-0.27
130.35	69.189	69.358	-0.24
144.52	65.543	65.207	0.51
149.27	64.026	63.567	0.72
153.71	62.059	61.865	0.31

TABLE V-39

V-39. Comparison of Eqn. V-19 and Saturated Liquid Density Values for R-502 Reported in This Work

t F	d lbs/cu.ft.	d_{eq} lbs/cu.ft.	Percent Deviation
-161.80	104.220	104.219	0.00
-67.32	94.410	94.589	-0.19
32.00	82.560	82.642	-0.10
50.55	79.680	80.033	-0.44
60.25	78.500	78.595	-0.12
63.79	78.020	78.055	-0.05
64.83	77.940	77.895	0.06
102.01	71.580	71.573	0.01
116.25	68.760	68.718	0.06
157.86	57.290	57.101	0.33
168.78	52.240	51.715	1.00
176.22	46.270	44.926	2.90

TABLE V-40

V-40. Comparison of Eqn. V-19 and Saturated Liquid Density Values for R-502 Reported by Badylkes (5,6,7)

t F	d lbs/cu.ft.	d_{eq} lbs/cu.ft.	Percent Deviation
-112.00	100.530	99.284	1.24
-103.00	99.090	98.362	0.74
-94.00	98.160	97.428	0.75
-85.00	97.240	96.483	0.78
-76.00	96.190	95.525	0.69
-67.00	95.160	94.554	0.64
-58.00	94.160	93.569	0.63
-49.00	93.170	92.568	0.65
-40.00	92.080	91.552	0.57
-31.00	91.130	90.518	0.67
-22.00	90.080	89.464	0.68
-13.00	89.050	88.391	0.74
-4.00	88.050	87.294	0.86
5.00	86.950	86.174	0.89
14.00	85.870	85.027	0.98
23.00	84.820	83.851	1.14
32.00	83.680	82.642	1.24
41.00	82.470	81.397	1.30
50.00	81.180	80.113	1.31
59.00	80.030	78.783	1.56
68.00	78.620	77.403	1.55
77.00	77.360	75.964	1.81
86.00	75.850	74.457	1.84
95.00	74.320	72.872	1.95
104.00	72.510	71.192	1.82

TABLE V-41

V-41. Comparison of Eqn. V-19 and Saturated Liquid Density Values for R-502 Reported by Loffler (86)

t F	d lbs/cu.ft.	d_{eq} lbs/cu.ft.	Percent Deviation
-112.00	99.720	99.284	0.44
-103.00	98.780	98.362	0.42
-94.00	97.850	97.428	0.43
-85.00	96.790	96.483	0.32
-76.00	95.890	95.525	0.38
-67.00	94.870	94.554	0.33
-58.00	93.880	93.569	0.33
-49.00	92.760	92.568	0.21
-40.00	91.800	91.552	0.27
-31.00	90.740	90.518	0.25
-22.00	89.570	89.464	0.12
-13.00	88.550	88.391	0.18
-4.00	87.430	87.294	0.16
5.00	86.230	86.174	0.06
14.00	85.050	85.027	0.03
23.00	83.910	83.851	0.07
32.00	82.680	82.642	0.05
41.00	81.390	81.397	-0.01
50.00	80.140	80.113	0.03
59.00	78.820	78.783	0.05
68.00	77.450	77.403	0.06
77.00	75.950	75.964	-0.02
86.00	74.500	74.457	0.06
95.00	72.930	72.872	0.08
104.00	71.260	71.192	0.10
113.00	69.520	69.399	0.17
122.00	67.630	67.464	0.25
131.00	65.640	65.348	0.44

TABLE V-41 (contd.)

140.00	63.380	62.991	0.61
149.00	60.850	60.288	0.92
158.00	57.860	57.045	1.41
167.00	54.100	52.782	2.44
176.00	48.210	45.253	6.13

TABLE V-42

V-42. Comparison of Eqn. V-19 and Saturated Liquid Density Values for R-502 Reported by Du Pont (47)

t F	d lbs/cu.ft.	d_{eq} lbs/cu.ft.	Percent Deviation
-100.00	98.490	98.052	0.45
-80.00	96.550	95.952	0.62
-60.00	94.520	93.789	0.77
-40.00	92.490	91.552	0.92
-20.00	90.180	89.228	1.06
0.0	87.840	86.800	1.18
20.00	85.390	84.246	1.34
40.00	82.800	81.538	1.52
60.00	80.040	78.633	1.76
80.00	77.070	75.469	2.08
100.00	73.800	71.951	2.50
120.00	70.080	67.908	3.10
140.00	65.590	62.991	3.96
160.00	59.490	56.214	5.51

TABLE V-43

V-43. Comparison of Rectilinear Diameter Eqn. V-20 with Data For R-22

t F	d lbs/cu.ft.	d_{eq} lbs/cu.ft.	Percent Deviation
429.67	43.500	43.407	0.21
439.67	43.080	42.954	0.29
449.67	42.630	42.501	0.30
459.67	42.180	42.047	0.31
469.67	41.710	41.594	0.28
479.67	41.260	41.140	0.29
489.67	40.790	40.687	0.25
499.67	40.310	40.234	0.19
509.67	39.830	39.780	0.13
519.67	39.370	39.327	0.11
529.67	38.890	38.873	0.04
539.67	38.420	38.420	0.00
549.67	37.930	37.966	-0.10
559.67	37.470	37.513	-0.12
569.67	37.000	37.060	-0.16
579.67	36.530	36.606	-0.21
589.67	36.090	36.153	-0.17
599.67	35.620	35.699	-0.22
609.67	35.150	35.246	-0.27
619.67	34.690	34.793	-0.30
629.67	34.230	34.339	-0.32
639.67	33.750	33.886	-0.40
644.67	33.500	33.659	-0.47
649.67	33.300	33.432	-0.40
654.67	33.050	33.206	-0.47
659.67	32.550	32.979	-1.32

TABLE V-44

V-44. Comparison of Rectilinear Diameter Eqn. V-21 With Data for R-115

t F	d lbs/cu.ft.	d_{eq} lbs/cu.ft.	Percent Deviation
429.67	47.900	47.937	-0.08
439.67	47.420	47.420	0.00
449.67	46.940	46.903	0.08
459.67	46.440	46.387	0.11
469.67	45.940	45.870	0.15
479.67	45.410	45.354	0.12
489.67	44.890	44.837	0.12
499.67	44.350	44.320	0.07
509.67	43.800	43.804	-0.01
519.67	43.250	43.287	-0.09
529.67	42.710	42.770	-0.14
539.67	42.190	42.254	-0.15
549.67	41.680	41.737	-0.14
559.67	41.200	41.221	-0.05
569.67	40.730	40.704	0.06
579.67	40.200	40.187	0.03
589.67	39.710	39.671	0.10
599.67	39.290	39.154	0.35
609.67	38.700	38.637	0.16
614.67	38.420	38.379	0.11
619.67	38.150	38.121	0.08
624.67	37.800	37.863	-0.17
629.67	37.300	37.604	-0.82

CHAPTER VI

SUMMARY AND CONCLUSIONS

This work may be summarized in three parts. The experimental part consists of PVT determinations, vapor pressure measurements, saturated liquid density determination and observation of critical temperature for the azeotrope R-502. The second part consists of algebraic correlations of these properties. Best correlating equations for R-502 were evaluated first. Then the components' data were correlated to the same algebraic expressions which enabled prediction of the properties of the mixture R-502. Finally second virial coefficients of the components R-22 and R-115 as well as the mixture R-502 were used in evaluating two characteristic molecular parameters of the potential energy of interaction by a new analytical method. Combining rules for the parameters were tested.

PVT measurements for the azeotrope R-502 covered a temperature range of 100 to 250 F, pressure range of 80 to 2000 psia and densities up to two times the critical density. An improvement in volume calibrations was obtained by using mercury as the hydraulic fluid. The volume of the bellows PVT cell is believed to be known within ±0.50% while Bhada (15) reported a value of ±1.3%. Due to improvements in insulation of the bath, heater capacities and heater placements, temperature of the bath was controlled to within ±0.04 F. Using a more sophisticated dead weight gauge of Ruska, pressure gauges were calibrated to an accuracy of 0.1 %. Overall experimental accuracies are as follows: specific volumes: +0.50%, temperature values +0.04% and pressure values ±0.17%.

Low vapor pressure determinations for R-502 ranged from -100 to -40F covering a range of 0.4 psia to 16 psia. Temperature control was of the order of ±0.1F. Experimental vapor pressure values are believed to be precise to ±0.04 psi. High vapor pressure values were obtained using the PVT cell covering a temperature range of 100 F to the critical temperature. Precision in pressure and temperature values is the same as that given above for PVT determinations.

Saturated liquid density of R-502 was determined over a range of -160 to 176 F. Temperature control at the low temperatures was of the order of ±0.1Fand at the high temperatures of the order of ±0.04 F. The density values are believed to be accurate to ±0.1%. Critical temperature was observed using an appropriate saturated liquid density bulb and is believed to be precise to ±0.2 F.

The Martin-Hou (91) equation of state is improved and used to correlate the PVT data for the mixture. The equation of state is capable of predicting volumetric data up to 1.8 times the critical density. The experimental data are correlated to an average deviation of -0.23%, average absolute deviation of 0.60% and standard deviation of 0.95%. Vapor pressure data and saturated liquid density values are correlated by Martin and Downing (90). Vapor pressure of R-502 was correlated to an average deviation of -0.22% and average absolute deviation of 1.28%. The saturated liquid density of R-502 was correlated by Martin and Downing (90) with an average deviation of +0.075% and average absolute deviation of 0.11%. Using the critical temperature of R-502 to be 639.56 R, Martin and Downing (90) determined the critical pressure of 591.0 psia. They also reported the critical density of 35.0 lbs/cu.ft, which was confirmed in this investigation by the analysis of the data.

Using the improved equation of state PVT data available in the literature for the components of the mixture, namely R-22 and R-115 were correlated. Using the generalized approach input conditions to evaluate the constants in the equation of state were determined. These input conditions were combined on a mole fraction basis and used with combined critical constants in order to predict the PVT behavior of R-502. The predicted values compare very well with the experimental data over the entire range except around the critical point and at extremely high densities. Similarly, the vapor pressure equation given by Martin, Kapoor and Shinn (93) is transformed into reduced form and these reduced constants were evaluated for R-22 and R-115 using the literature data. Constants of the vapor pressure equation were combined on the basis of factor M (91) along with the combined critical constants to predict the vapor pressure of R-502. The prediction is good in the intermediate pressure ranges but is in error

at low pressures and near the critical temperature. The saturated liquid density data available in the literature for R-22 and R-115 is correlated with the Martin-Hou eqn. (91). Constants in the equation were reduced and combined on a mole fraction basis, which in turn were used to predict the saturated liquid density data. The prediction is excellent everywhere except within a few degrees of the critical temperature. A literature search was made to find accurately determined critical constants of R-22 and R-115. Several methods of prediction of critical constants of mixtures were reviewed. Li, Chen and Murphy (85b) method of prediction of critical temperature method was found to be the best. This method utilizes an extra piece of information, namely the normal boiling point. Critical volume of the mixture was best predicted by averaging , on a mole fraction basis, the critical volumes of R-22 and R-115. A new method of predicting the critical pressure of the mixture is proposed. The method is empirical, but simple.

The second virial coefficients for the mixture R-502 and components R-22 and R-115 at three temperatures (T_R = 0.8, 1.0, 2.3) were a by-product of the PVT correlations. From these two characteristic molecular parameters, U_m and d_m of the potential energy of interaction were determined by a new analytical method. Algebraic handling is very easy and the order of magnitude of the parameters is very close to that determined by other realistic methods which are usually tedious and complicated. An extensive literature review on this subject is presented and it reveals that this approach is the first of its kind. The component parameters were combined using well known rules to predict the second virial coefficients of the mixture. The prediction was good considering the accuracy in the second virial values.

In conclusion, PVT data is obtained to a better precision than that obtained before by Bhada (15) using the same PVT cell. An extremely improved equation of state has been developed to predict the PVT behavior of substances. A new rule for the prediction of true critical pressure of azeatropic mixtures of halogenated hydrocarbons is developed.

A new analytical method to evaluate the intermolecular potential (Martin) energy parameters is presented.

CHAPTER VII

RECOMMENDATIONS FOR FUTURE WORK

Several improvements can be made in the present investigation. In experimental methods the simplest recommendation is to improve the temperature control techniques for low pressure determinations. A major recommendation is to improve the volume calibration of the bellows PVT cell. Detailed information on Bridgman bellows PVT cell (23) is given in Chapter II which suggests that by employing an extremely well machined screw to measure the change in the bellows position, an improvement in the volume calibration may be obtained. In order to have a duplicate check on volume calibration, a sophisticated mercury pump as used by Keyes (73) and Beattie (8) may be incorporated in the system. Finally if the volume calibrations are determined accurately, simultaneous observation of isometric and isothermal PVT data would be possible.

The equation of state can be further extended to higher densities keeping in mind that addition of one extra exponential term in Eqn. (V-1) may cover succeedingly smaller ranges of density. Reduced vapor pressure equation may be modified to incorporate the factor M for completely generalized correlation. Further, the methods advocated here for the prediction of critical properties may be tested for other halogenated hydrocarbon mixtures.

Extremely promising is the new analytical method (should be called henceforth as the Martin method) of evaluating intermolecular potential energy parameters. This method should be tested with other accurate second virial coefficient data and compared with commonly used methods such as Lennard-Jones (12-6) potential (85).

APPENDICES

APPENDIX A

DETAILS OF TEMPERATURE AND PRESSURE MEASUREMENTS FOR PVT BEHAVIOR

AI. TEMPERATURE CONTROL SYSTEM:

Temperature of a bath was controlled by an on-off control. The bath was a jacketed steel vessel with an inside diameter of 20" and a height of 18". The 3" thick jacket was filled with glass wool in order to insulate the bath fluid. Mineral oil was used as the bath fluid. The bath was equipped with two heaters coming out of its bottom and placed diagonally across each other. Their heating capacity was 1000 watts each. A half horsepower stirrer could be mounted off-center on the bath to give vigorous stirring of bath fluid. In addition to these heaters, a knife heater of 250 watts capacity was used, whose output was controlled by a Variac.

The temperature sensor was a dot $_y$ magnet thermoregulator. This thermoregulator (Fig. A.-1) has an adjustable wire contact with mercury. The dot magnet "D" connected to contact wire "C" can be rotated as desired by an outside ring magnet "E". Contact wire "C" touches the mercury in capillary "F". Capillary "F" ends in a hugh bulb "G" filled with mercury. Depending on the temperature desired, the amount of mercury in "F" and "G" can be overflowed or added. Cavity "H" serves as another auxilliary reservoir for mercury. The space above the mercury is filled with inert gas. The two leads coming out of the regulator are connected to a relay circuit. The range of temperature control is -30 to + 350 F. Temperature of the bath was controlled to ±0.04 F by using continuous heat input of knife heater and on-off controlled heat input through regulator-relay-heater circuit.

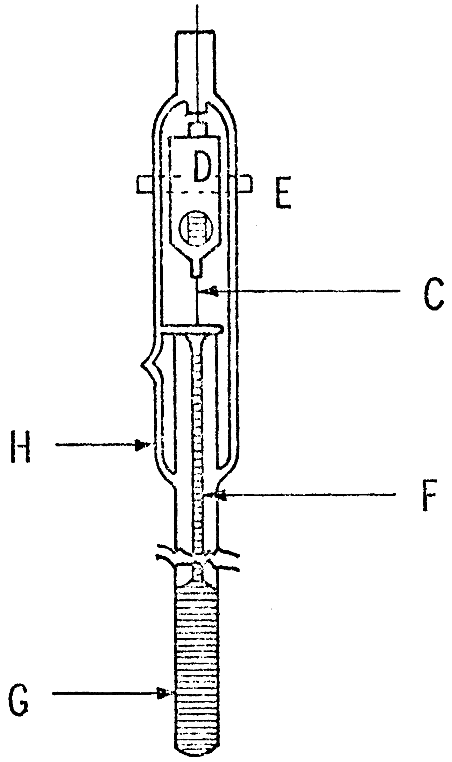

Fig. A1. Doty Magnet Adjustable Thermoregulator

In conjunction with the doty magnet thermoregulator, a relay (Cat. No. 4-5300) supplied by American Instrument Company, was used. Installation of the relay is schematically presented in Fig. A-2. Relay circuit is given in Fig. A-3 specifications of the relay were:

Power requirement: 118/208/230 Volts ±10%, 50/60 cycles a.c.,
17 Voltamperes.

Control Circuit: a) Open circuit potential 12 volts a.c.
b) Current on shorting control terminals = 10 ma.
c) Characteristics: Control contacts resistance must be less than 25 ohms.
d) Maximum control circuit lead length limited by cable capacitance of 2 MFD max, or resistance of 25 ohms max.

Any one or more heaters can be connected to the relay. Knife heater output was adjusted by varia_c so that roughly 3 to 4 on-off contacts per minute were obtained. At the highest temperature, control was accurate within ±0.04 F and for other temperatures usually less than ±0.03F.

AII. TEMPERATURE MEASUREMENT SYSTEM

Platinum Resistance Thermometer-Potentiometer-galvanometer assembly was obtained from Leeds and Northrupt Company and was used to measure temperature within 0.001 C.

Platinum resistance thermometer (Cat. No. 8163-c) is a four terminal-type thermometer in which "potential" leads are joined with "current" leads at branch points. There are four coils each having a branch point at its ends and resistance of the coil is the resistance included

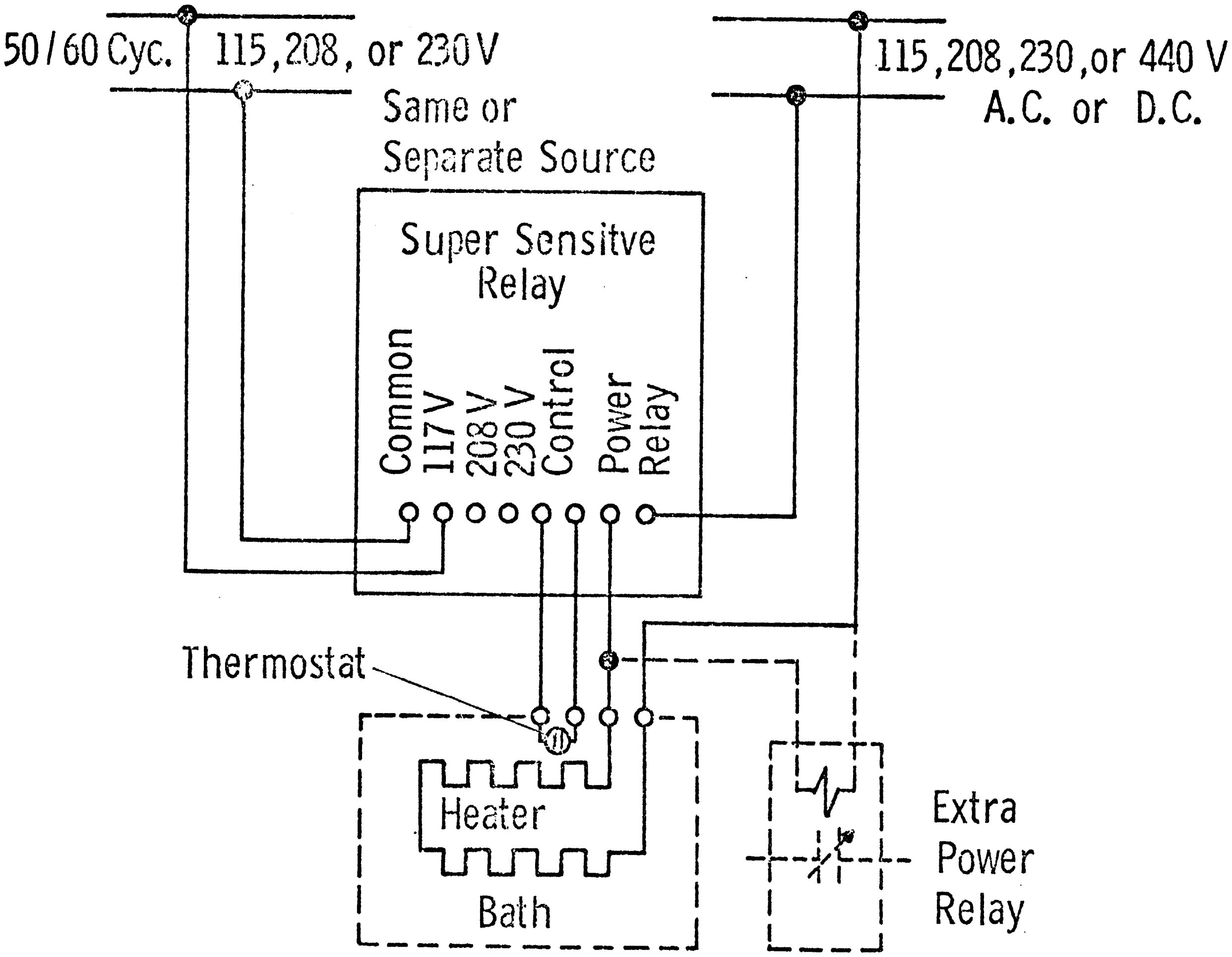

Fig. A.2 Supersensitive Relay Installation

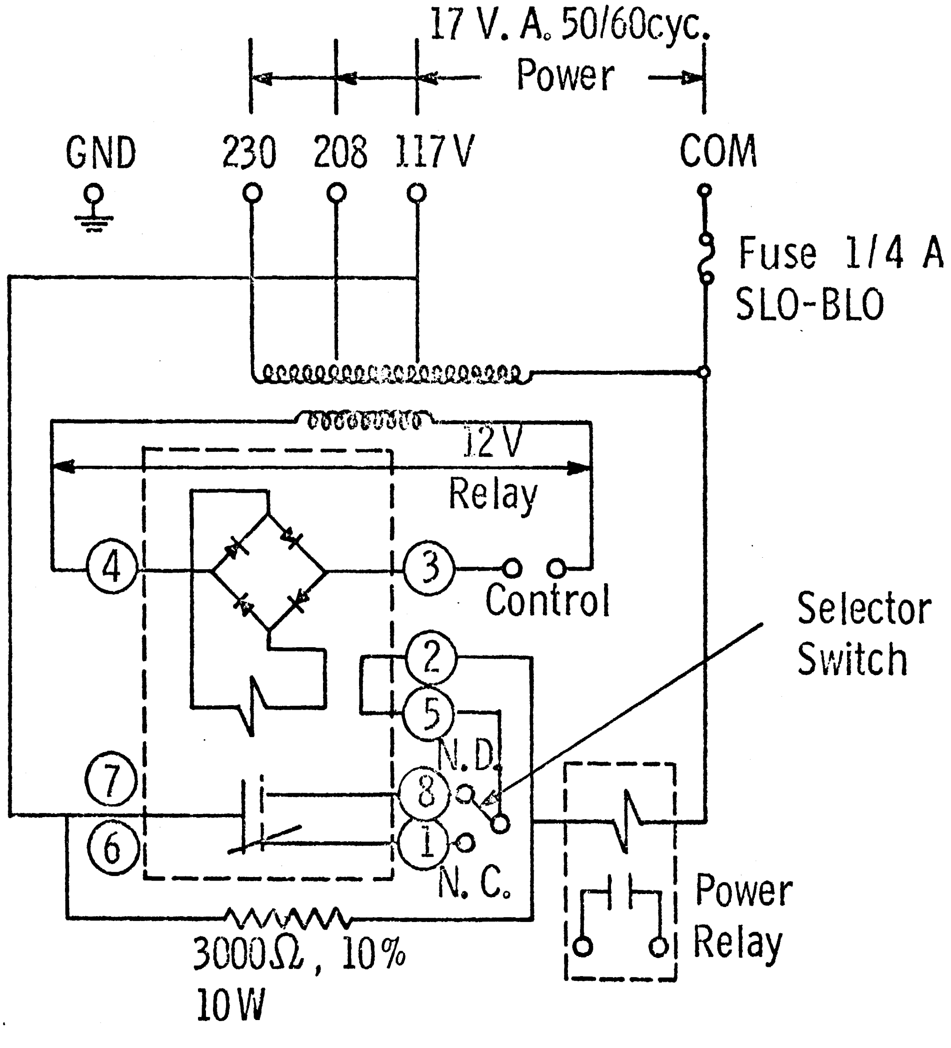

Fig. A.3 Schematic of Relay Circuit

between the branch points. All coils are encased in a high conducting glass tube, with four leads going to a potentiometer.

The potentiometer, Ser. No. 1327006, was a 8067 type G-1 Mueller bridge (A-2). It measures resistance between 0 and 81.111 ohms in steps of 0.0001 ohm., which covers the entire temperature range of 8163-c platinum resistance thermometer. Without ambient temperature correction, resistance can be measured within an error of a few ten thousands of an ohm or ±0.02%. In conjunction with this potentiometer, a galvanometer, Cat. No. 2430, Type E, was used to obtain null points. This galvanometer has an enclosed lamp and 10 cm. wide scale. There are two light spots on the scale, a primary split by an index and a secondary split to show direction of deflection. Deflections are linear within one percent. The galvanometer operates with a power supply of 115 volts, 50/60 cps. Galvanometer, Ser. No. 1209153, has a sensitivity of 43 μv/MM, period of 3.2 sec. and 16 ohms resistance. Other equipment was an 8068 L&N type commutator, Ser. No. 1511595, and four dry cells. Complete circuit diagram of the temperature measuring system is given in Fig. A-4.

8163-c type platinum resistance thermometer covers the temperature range of -190 to +500 c. Resistance of this thermometer can be easily expressed in terms of international temperature scale by the Callender formula. For temperature above 0 C:

$$t = \frac{R_t - R_o}{\alpha R_o} + \delta\left(\frac{t}{100} - 1\right)\frac{t}{100} \qquad \text{(A-1)}$$

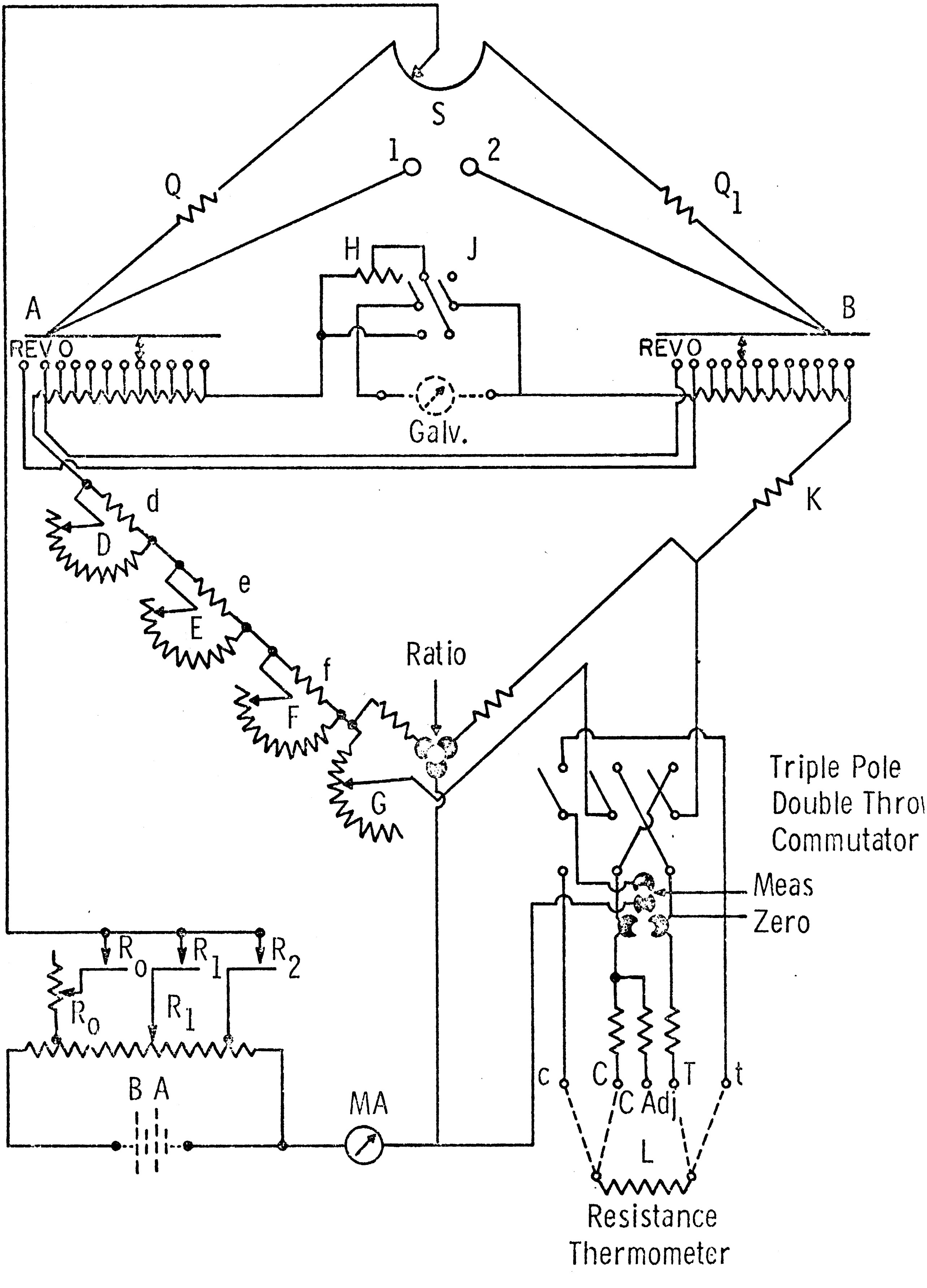

Fig. A.4 Circuit Diagram for Temperature Measuring System where t = temperature in C

R_t = resistance at temperature t

R_o = resistance at 0 C

R_{100} = resistance at 100 C

$\alpha = \frac{R_{100} - R_o}{100\ R_o}$ = characteristic constant of the thermometer

δ = another characteristic constant of the thermometer.

Constant α is determined from R_{100} and R_o while δ is determined usually from the calibration at the boiling point of sulphur. For temperatures below 0 C, Eqn. A-1 is modified as:

$$t = \frac{R_t - R_o}{\alpha R_o} + \delta\ (\frac{t}{100} - 1)\ \frac{t}{100} + \beta\ (\frac{t}{100} - 1)\ (\frac{t}{100})^3 \qquad \text{(A-2)}$$

where β , one more characteristic constant of the thermometer is determined by calibration at the boiling point of oxygen. For convenience in use, Eqn. A-2 can be written as:

$$\frac{R_t - R_o}{R_o} = \alpha\ [t-\delta(\frac{t}{100} - 1)\ \frac{t}{100} - \beta\ (\frac{t}{100} - 1)\ (\frac{t}{100})^3\ ] \qquad \text{(A-3)}$$

Eqn. A-3 can be used to prepare calibration tables of R_t vs. t every one degree apart. Linear interpolation of resistance to evaluate temperature from values which are one degree apart, involves an error of less than 0.001 C. Two platinum resistance thermometers were used in the experimental work, whose characteristic constants are certified by the National Bureau of Standards and are given in Table A-1.

TABLE A-1

CHARACTERISTIC CONSTANTS IN EQN. A-3 FOR PLATINUM RESISTANCE THERMOMETERS

Constant	Thermometer	Serial Number
R_o	25.543	25.505 abs.ohms
α	0.003926395	0.0039264_{72}
β	0.110_{20}	0.110_{24}(below 0 C)
β	0.000	0.000 (above 0 C)
δ	1.491_{59}	1.491_{60}

The thermometer with Ser. No. 1504255 was checked for its ice point and steam point (using a hypsometer) and resistance values were found to duplicate those given by NBS within the accuracy of G-1 type Mueller bridge. The second thermometer was not checked since the data of certification was very recent.

With on-off control described in the previous section, temperature of the bath fluctuates in a sinusoidal fashion (Fig. A-5). This was clearly noticeable on the galvanometer scale where at worst, the hair index traversed a path between the middle 8 cm region. Two centimeters on the galvanometer scale roughly amounted to about 0.01 C. At any time, resistance R_{av} was recorded in data books, whether commutator position was in normal (N) or reverse (R) setting. Assuming temperature of the PVT cell to be the average value T_{av}, uncertainty in T_{av} amounts to ± 0.02 C or ± 0.04 F.

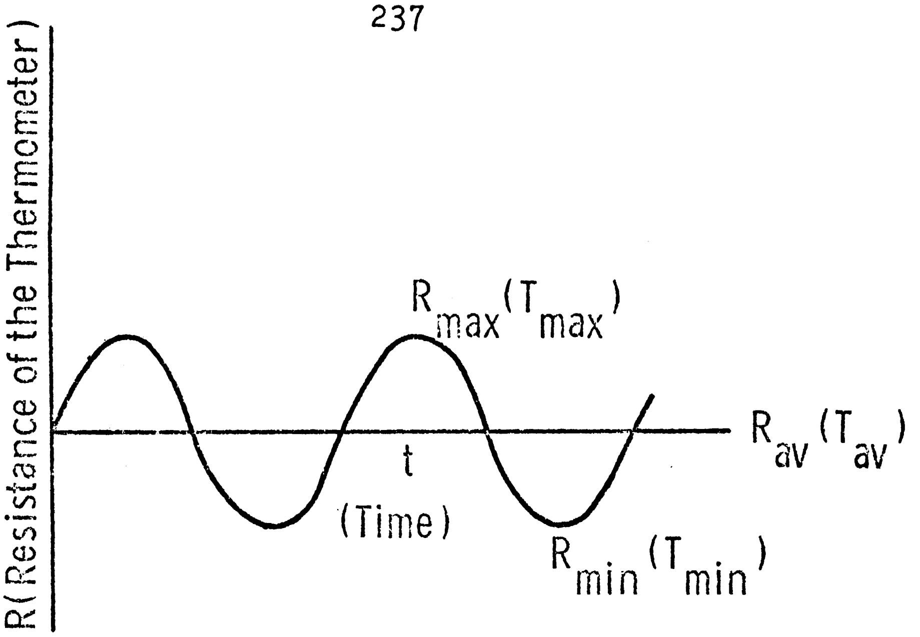

Fig. A. 5. Temperature Fluctuations of the Bath

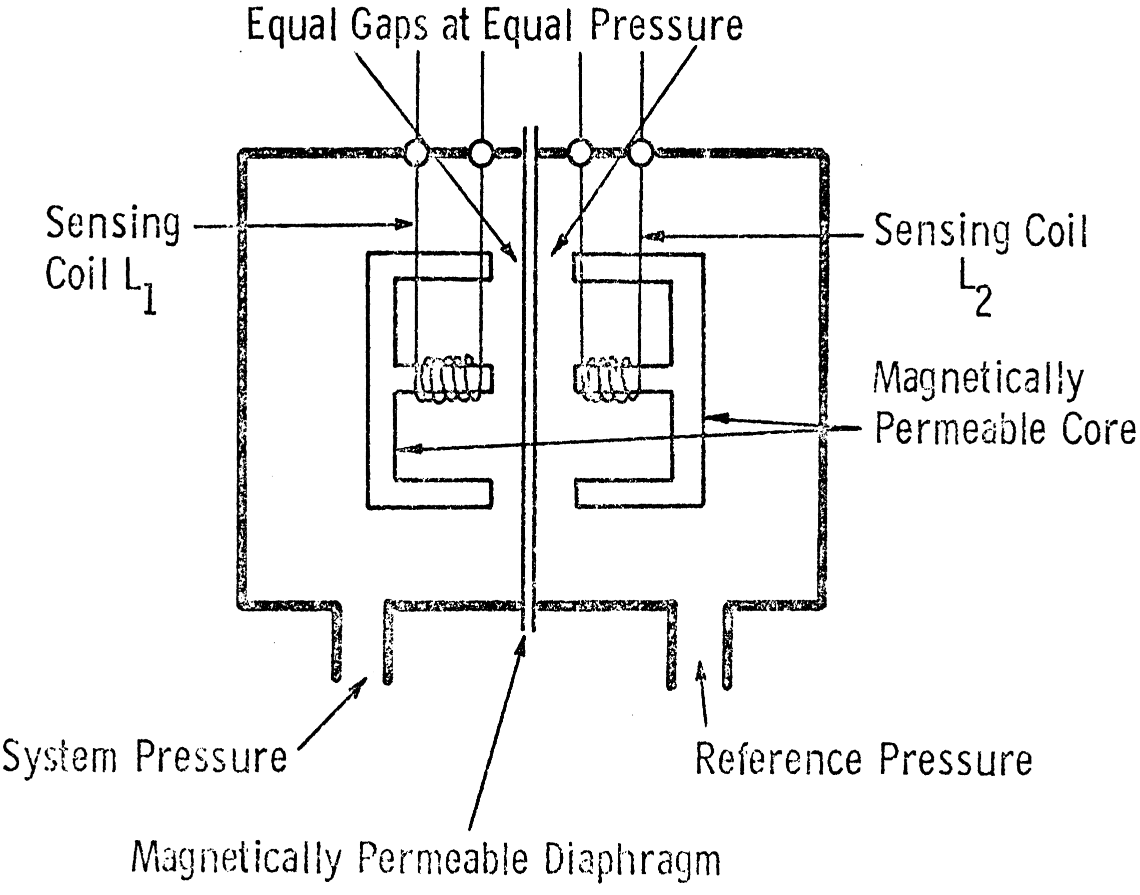

Fig. A. 6. Pace - Diaphragm Pressure Transducer

AIII. MEASUREMENT OF PRESSURE

The pressure measuring system consisted of a nitrogen tank serving as a pressure source to Bourdon gauges. Three Bourdon gauges were connected to a pressure transducer which in turn was connected to the PVT cell.

A nitrogen tank supplied the highest pressure of measurement of about 2000 psia. Three Bourdon gauges of ranges and series numbers as follows were used:

Pressure Range in psi	Serial Number
0-100	H 21471
0-500	H 21470
0-2000	H 26058

The pressure gauges were always calibrated before and after experimental runs. Hysteresis losses were insignificant to show any changes on duplicating pressure readings. They were calibrated "in situ" by a Ruska dead weight gauge, Cat. No. 2400 HL, Ser. No. 13919. A Ruska dead weight tester has a precision of 0.1 psi at 2000 psi.

PACE - Pressure Transducer:

PACE - Pressure Transducer system consisted of a model KP 15 transducer and model CD 25 transducer indicator. Pressure measurements are based on the magnetic reluctance principle. This system offers the following advantages:

1) Dynamic response characteristic of this system is excellent either in liquid or in a gas system due to low volumetric displacement, low internal volume, and high natural frequency.

2) Corrosive liquids and gases can be used on both sides without isolation of pickoff mechanism.

3) Overload tolerance (200 psi) is relatively high, making it operator proof.

4) Severe shocks and vibrations can be with stood easily by the whole system.

5) Due to simple, self contained solid state circuitry, D.C. output level is high with unregulated 115 VAC or 28 VDC.

PACE - Pressure transducer is shown in Fig. A-6. A magnetically permeable, stainless steel diaphragm is clamped between two blocks and deflects if there is an imbalance of pressure. Pressures to the diaphragm are applied through the ports shown. In each block an E core and coil assembly is embedded such that a small amount of gas is left between the diaphragm and the E core. Arrangement is symmetrical so that in an undeflected position of the diaphragm, condition of equal inductance is obtained. Diaphragm deflection results in an increase in gap in the magnetic flux path of one core and equal decrease in the other. Variation in gap results in changing magnetic reluctance, thereby determining the inductance value. Thus deflection of the diaphragm results in increasing inductance of one coil while decreasing that of the other coil.

A bridge circuit for converting coil inductance ratio into D.C. output voltage is given in Fig. A-7. Four arms of the bridge are given by inductance coils L_1, L_2, and resistances R_1 and R_2. The bridge can operate on half cycles due to insertion of diodes in the resistive voltage divider. A potential is established at point B, during half cycle when diodes do not conduct, there is no output. Therefore, the output is half-cycle pulses. If voltages at point A and B are equal, output is zero, while if potential at A is larger than that at B, the output has one polarity. Similarly if voltage at A is less than that at B, output polarity reverses. The ratio $\Delta L/(L_1+L_2)$ is usually 5% at full scale in typical transducers, corresponding to output voltage of 50 mv per volt of excitation. The effect of filter on bridge output is shown in Fig. A-8.

Model KP 15 pressure transducer, Ser. No. 21052, with a diaphragm range of ±25 psi was used. Hysteresis was about ±0.3% for pressure excursion. The transducer had a specified range of temperature operation of -423 to +250 F. Between -65 to +250, zero shift coefficient was within 0.01% and sensitivity coefficient within 0.02% of full scale per degree F. Therefore, sensitivity of the transducer, at worst, was better than 0.01 psi. However, null point changed with temperature amounting to a drift of about 0.5 psi at the highest temperature of 250 F.

The PACE - pressure transducer assembly was used as a null indicator. Pressures were read accurately on calibrated Heise gauges. Error contribution can be divided as:

1) Precision of Heise gauges.
2) Accuracy of the dead weight tester.
3) Precision in calibration of the Heise gauges.
4) Precision in transducer sensitivity.

Precision of the Heise gauges was claimed by the manufacturer

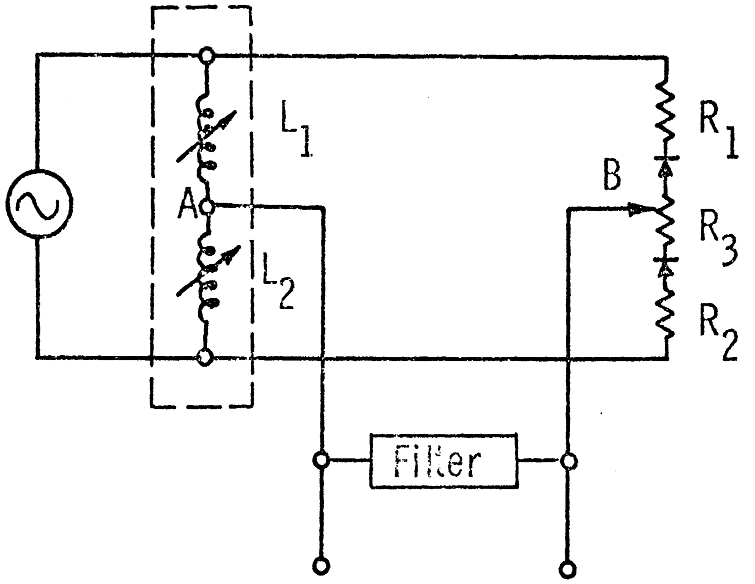

Fig. A.7 Bridge Circuit to Convert Coil Inductance Ratio into DC Output Voltage

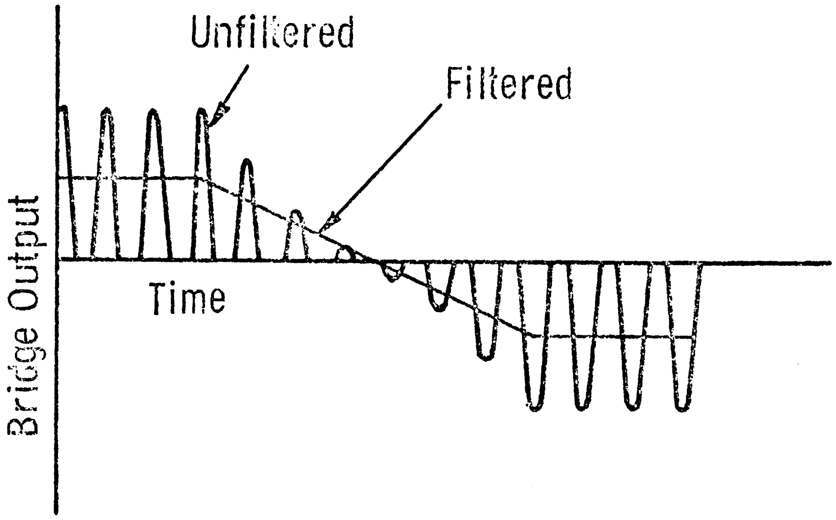

Fig. A.8 Bridge Output with and Without Filter as +0.1%. Manufacturer of the Ruska dead weight tester claimed an accuracy of ±0.01% of the reading. Precision in calibration was ±0.05% of the reading. Precision in transducer sensitivity was ±0.01%. The pressure values are believed to be accurate to ±0.17%.

APPENDIX B

DETAILS OF VOLUME CALIBRATION

The volume of bellows cell is calibrated as a function of height. In order to obtain this function, PVT measurements were made on carbon dioxide whose PVT behavior is well known (57, 101). These measurements ranged over 80 to 250 F and up to 2000 psia. The experimental procedure is the same as that described for obtaining PVT measurements (Chapter III). In this section we shall illustrate analysis of the data.

Volume of the bellows is a function of 1) compressibility of the hydraulic fluid due to pressure, 2) contraction or expansion of the hydraulic fluid due to temperature and 3) contraction or expansion of the cylinder due to temperature. All these effects could be incorporated to give the expression for volume as follows:

$$V_{h,T,P} = (V_h)_{T_o,P_o} + \{(\frac{\Delta V}{\Delta P})_{h_o,T}(P-P_o) + (\frac{\Delta V}{\Delta T})_{h_o,P}(T-T_o)\}\ y_h \qquad \text{(B-1)}$$

where

$V_{h,T,P}$ = volume of the bellows at any height, temperature and pressure

$(\Delta V/\Delta P)_T$ = variation of volume with pressure

$(\Delta V/\Delta T)_P$ = variation of volume with temperature

P = pressure, psia

P_o = reference pressure, psia

T = temperature, R

T_o = reference temperature, R

h_o = reference height

y_h = a factor accounting for the variation of temperature and pressure coefficients with height

In our case the hydraulic fluid is mercury for which temperature effects are large compared to pressure effects.

During the preliminary observations our hydraulic pump leaked mercury during compressing. With help of the supplying company we changed gaskets around the piston and inserted improved glands where at least **during** one run we could not obtain mercury leaks. All the minute amounts of leaked mercury were collected carefully and added to the reservoir tube. This put a severe limitation on our data collection. Experimental procedure was to make both volume calibration and PVT observations on R-502 at the temperature of the isotherm successively and within a period before which the piston gaskets would give up under stress.

Thus the data is analyzed at the given temperature only. All the experimental data is listed in Table E-2. The data analysis showed that volume of the bellows could be expressed as a function of height only at a given temperature. Therefore we formulated the following equation:

$$V_h - m\,h + C \tag{B-2}$$

where

V_h = volume of the bellows cell

m = slope factor (dV/dh) in^3/cm

C = constant.

As an example let us take the isotherm at T = 708.94 R. At this temperature, volume of the bellows is given by the following equation:

$$V = 0.529063\ h + 20.8449 \qquad \text{(B-3)}$$

Eqn. (B-3) is compared with the volumetric data of carbon dioxide in Table B-1.

TABLE B-1

Comparison of Eqn. (B-3) with the Volumetric Data of Carbon Dioxide

Obs. No.	h cm	V_{exp} in^3	V_{calc} (Eqn.B-3) in^3	Percent Deviation
C47	98.855	73.26	73.15	+0.15
C48	72.860	59.42	59.39	+0.05
C49	49.00	46.74	46.77	-0.06
C50	26.92	35.09	35.09	0.00
C51	13.70	28.08	28.09	-0.04
C52	2.785	22.31	22.32	-0.05

Average absolute deviation = 0.06%

Average deviation = +0.01%

All the data was analyzed in this fashion and the constants in Eqn. (B-2) with their comparisons to experimental data are summarized in Table B-2.

TABLE B-2

Constants in the Eqn. (B-2) and Its Comparison with the Experimental Data of Carbon Dioxide

T R	M in^3/cm	C in^3	Av.Ab. % Dev.	Av. %Dev.	Max. %Dev.
541.1	0.521614	22.2134	0.08	-0.04	±0.20
639.6	0.53645	21.7472	0.12	+0.04	±0.17
664.1	0.529047	21.5752	0.09	-0.01	±0.11
666.1	0.533289	21.2997	0.07	-0.01	-0.12
708.9	0.529063	20.8449	0.06	+0.01	+0.15
711.4	0.529506	20.9197	0.06	0.00	+0.10

Experimental Precision

The mercury level measurement readings should be accurate to ±0.001 cm which amounts to a volume of about 0.0053 cu.in. At the smallest bellows volume (about 22 cu.in.) this error amounts to ±0.03% and decreases to ±0.01% at the largest volume. The PVT behavior of carbon dioxide is known to ±0.05% and other experimental errors in temperature measurements, pressure measurements and mass recovery are estimated to be ±0.15%. Therefore at best the volumes obtained through calibration are accurate to ±0.20%. These volumes are correlated by the equation with the deviations of ±0.20%. Weight of the charging cylinder changes with the barometric pressure due to buoyancy. Maximum variation in the barometric pressure during our runs was of the order of ±6 mm. This barometric pressure variation gives rise to an error of ±6 mg. This amounts to an error of ±0.02% for lowest sample weight to ±0.001% for the highest sample weight. Sample recoveries were within ±0.03%. Calibrated weights were used which were believed to have an accuracy of ±0.01%. The accuracy of the whole weighing procedure was estimated to be ±0.05% for the smallest sample. The specific volumes reported are estimated to be accurate to ±0.5% at the lowest bellows volumes and ±0.25% at the highest bellows volume.

APPENDIX C

DETAILS OF VAPOR PRESSURE MEASUREMENTS

These measurements covered the pressure range of 0.7 to 590 psia corresponding to the temperature range of -100 to 180 F. Using static method, Vora (138) made low vapor pressure measurements. High vapor pressures were obtained from the PVT measurements.

LOW VAPOR PRESSURE MEASUREMENTS

Experimental System:

A schematic presentation of the experimental system is given in Fig. III-3. The charging cylinder is a high pressure vessel of 500 cc capacity. A needle valve, V_1, controls the discharge from the cylinder. It is shown in an inverted position for the reasons given for charging PVT cells. Stainless steel tube 1/4" O.D. from value V_1 is connected to glass tubing by a steel to glass ball joint. A drying U tube was filled with P_2O_5. The line from the drying tube then divides, one going to the isoteniscope and the second to the mercury barometric leg. All lines are made of Pyrex glass 12 mm O.D. unless otherwise specified. From the barometric leg, a connection is taken which was used to fill the saturated liquid density bulbs. The mercury barometric leg serves as a pressure safety valve in the event that the system pressure exceeds one atmosphere through an accident. Valve V_3 separates the isoteniscope completely from the drying tube and barometric leg. The isoteniscope is made of a 25 mm O.D. glass tube about 5" long. The isoteniscope is placed in a constant temperature bath. A dewar flask, about 6" I.D. and 10" high with two diagonally opposite 1/2" wide slits was used as a bath. It was equipped with an air driven stirrer, platinum resistance thermometer, a knife heater and a tube supplying liquid nitrogen cooled air. A platinum resistance thermometer was connected to the usual bridge galvanometer assembly. The isoteniscope is connected to the mercury U tube manometer, the legs of which can be isolated through valve V_4. Valve V_8 is the vent valve. One leg of the U tube manometer is connected to the vacuum system, which consists of a McLeod gauge, mercury diffusion pump and a mechanical vacuum pump. The McLeod gauge was capable of reading a vacuum of one micron of mercury. The levels of mercury in the legs of the U tube manometer were measured by a cathetometer capable of reading to an accuracy of 0.001 cm. Mercury in the manometer must be as clean as possible.

Procedure of Operation:

Referring to Fig. III-3, with valves V_1, V_7 and V_8 closed, others being completely open, the mechanical vacuum pump was started. The system is made leak proof, and within a few minutes, a vacuum of about 10 microns is obtained. Then a mercury diffusion pump is started which lowers the vacuum to less than 5 microns. Once the system is evacuated, with valves V_4, V_7 and V_6 closed, valve V_1 was cracked slightly. Pressure of about 2-3 psia was allowed to build up in the system and then the isoteniscope was cooled, first by dry ice and then by liquid nitrogen. The test sample, R-502, condenses in the isoteniscope. After making sure that the isoteniscope is about two-thirds full, valve V_1 was closed and sufficient time was allowed for any amount left in the lines to condense into the isoteniscope. Now valve V_3 was closed and the system is ready for the observation of the data. If by accident valve V_1 leaks, any pressure build up will be indicated by the mercury barometric leg. Or if V_2 is closed, with lines between V_2 and V_3 being under vacuum, the mercury barometric leg will show accordingly if valve V_3 leaks when pressure in the isoteniscope is of the order of 15 psia. During any experimental run the height of mercury in the barometric leg did not drop.

For measurements between -80 to -30 C, normal propanol was used as a bath fluid. Below -80 C, petroleum ether was the bath fluid. The temperature of the bath was controlled manually by setting the bubble rate of cooled air and heat input at different levels, resulting in a constant temperature of the bath. The temperature of the bath was continuously monitored by the resistance thermometer. After about 5 minutes of constant temperature condition, levels of mercury in the U tube manometer were recorded. One leg of the manometer is subjected to the vapor pressure of R-502 contained in the isoteniscope, and the other leg was exposed to a vacuum of less than 5 microns. Therefore the difference in the levels of mercury in the manometer legs directly gives the vapor pressure of R-502 at the bath temperature. No boil-off can be done since it would result in the fractionation of the mixture. In one run, several values of vapor pressure were obtained. This procedure was duplicated at least two times to make sure that all vapor pressure values are consistent. After every run R-502 was vented through valve V_8.

Due to some leaks on the vacuum pump side, Vora (138) used atmospheric pressure on one leg of the manometer to balance vapor pressure of R-502 in some readings.

Experimental Precision:

Temperature control during the runs were no better than ±0.1 F. For low vapor pressure measurements $\Delta P/\Delta T \simeq 0.3$ psi/F. This gives a possible error in the vapor pressure of ±0.03 psi due to temperature inaccuracies. Inaccuracy in the reading of mercury levels was estimated to be ±0.1 mm, giving the differences in the levels accurate to ±0.2 mm, corresponding to a pressure of ±0.005 psi. Therefore, the total error in the vapor pressure values is estimated to be ±0.035 psi.

Sample Calculations:

Data Point No. 18

Rav = 19.8559 ohms

h1 = 71.503 cm.

h2 = 43.873 cm.

B.P. = 737.40 mm.

for Rav = 19.8559 T = 217.76 K.

$$Ps = B.P. -(h_1 - h_2) = 461.1 \text{ mm} = 8.917 \text{ psia.}$$

$$\frac{h1 + h2}{2} = 57.688 \text{ cm.}$$

$$\frac{(h1 + h2)}{2}_{av} = 57.748 \text{ cm.}$$

: Possible error = 2(57.748 - 57.688) = ±0.12 mm = ± 0.003 psi. Error due to temperature fluctuations = ±0.05 x 0.3 = ± 0.03 psi. T = 217.76 K.

Vap. pr. = 8.917 ± 0.033 psi.

High Vapor Pressure Measurements:

The experimental system is the one used to obtain PVT data. On varying volume through the two phase region pressure was noted, which gave vapor pressure of R-502 at the temperature of the bath. Temperature control of the bath was within ±0.04 F amounting to a maximum error ($\Delta p/\Delta T = 7$ psi/F at the critical) of ±0.3 psi. Deviation of the vapor pressure points from the average value was of the order of ±0.6 psi. High vapor pressure values are estimated to be precise to ±0.17%.

APPENDIX D

DETAILS OF SATURATED LIQUID DENSITY MEASUREMENTS

Hossain (61) measured saturated liquid density of R-502 from -110 to +180 F. using a sealed glass tube containing a calibrated density float. Details of the measurements are given here.

Several density floats with different values of density were prepared. Each float was made of a Pyrex glass tube of about 6 mm I.D. and about one inch long, enlarged at one end in a bulb. After putting in some lead shots, the tube was sealed. Density of this float was determined by weighing it in the air and then in the distilled water.

One liquid density bulb was constructed for each density measurement. A high pressure Pyrex glass tubing, 15 mm O.D., 4 mm wall thickness was sealed at one end and a density float was placed in it. Then the tube was necked down to leave a bulb of about 4" long as shown in Fig. D-1.

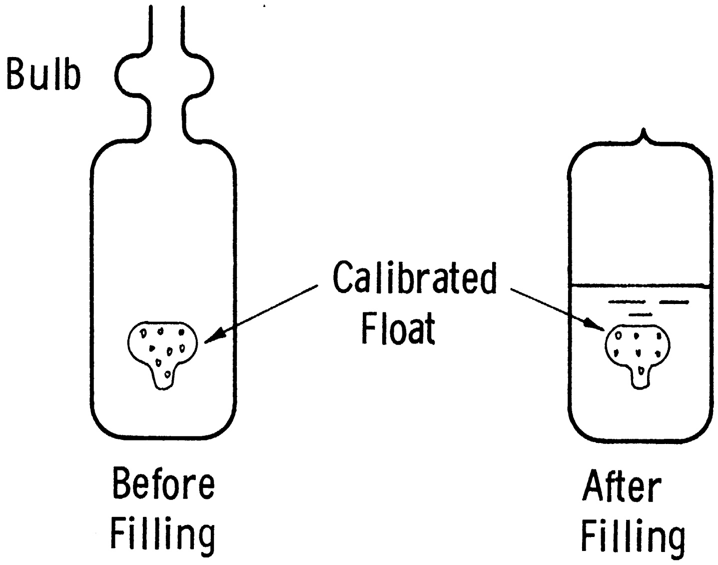

Fig. D-1. Saturated Liquid Density Bulb

The tube was necked down to about 3 mm I.D. and about 1" long. The tube was necked down again about 1" beyond the first neckdown leaving a bulb. Leaving a length of 2-3" from this bulb, the tube was cut off. The tube was annealed very carefully with a low temperature flame to remove any strain developed during its preparations. The number of the float is carved on the bulb between the necked down tubes.

Loading of the bulb was done using the apparatus for the vapor pressure measurements shown in Fig. III-3. After half filling the tube, it was sealed off at the lower necked down portion using a gas-oxygen torch. During the sealing process, the density bulb was held at liquid nitrogen temperature, where vapor pressure of R-502 is very small. Therefore, when the bulb was being sealed and the glass is soft, the wall presses inside due to atmospheric pressure. The sealed tip of the bulk was annealed with a low temperature flame. The loaded bulb is shown in Fig. D-1. Each loaded bulb was stored in a 1" I.D. and about 7" long iron pipe, screwed at both ends by caps and supplied with cushion cotton. Each storage pipe was marked with the float number used in the density bulb. The density bulbs were allowed to stand overnight to make sure that no leaks were present.

The experimental set up to measure saturated liquid density is shown in Fig. III-4. Here the temperature at which liquid density equals the float density was recorded. A unsilvered dewar flash about 10" I.D., 12" high was used as a bath. It was equipped with an air driven stirrer, knife heater and a supply of liquid nitrogen cooled air. The density bulb was suspended by a rubber tube. The whole assembly was put in a safety box and the safety box had a safety glass to watch the density float. The other 5 sides were made of steel and were painted black. A source of light was provided inside the box . Normal propanol was used as a bath fluid for temperatures up to -80 C, below which petroleum ether was used and for high temperature measurements, ethylene glycol was used as a bath fluid.

For a given density bulb, approximate temperature on a mercury thermometer at which float starts sinking or rising is found. Temperature of the bath is then controlled for at least 15 minutes to make sure that the test sample in the density bulb is at the bath temperature and that the pressure in the bulb does not break it. After taking this precaution, a shielded platinum resistance thermometer was inserted in the bath. Temperatures of the bath corresponding to rising and sinking of the float in the density bulb were recorded. The temperature control was such that these temperatures did not differ by more than 0.1 F. An average of these two temperatures were taken as the temperature at which density of the liquid equals density of the calibrated float. Density of the float was corrected for expansion of the glass tube due to temperature.

Experimental Precision:

The temperatures for rise and fall of the density float did not differ by more than 0.1 F. Therefore temperature values are believed to be precise to ±0.05 F. Calculations indicated that such a temperature error would amount to the accuracy in the liquid density of about ±0.02%. The densities of the floats were calibrated by weighing them in air and then in water. The weights of the floats in the air were considered accurate to within 0.0001g out of approximately 1 to 3.5 grams. The weights of the floats immersed in water were reproducible within 0.0002 grams. The possible errors of the volumes of the gloats were less than 0.01% or 0.0001 cc out of the total volume of about 1.0 cc. Estimated precision in the float density values is ±0.03%. The float densities were corrected for temperature changes.

The density float is subjected to vapor pressure of the azeotropic mixture. To evaluate the effect of pressure on volume changes the float may be considered as a thick walled cylinder of 6mm I.D. and 2mm. thickness. Then the change in the outer radius r_2 is given by the following equation:

$$\Delta r_2 = -\frac{r_2 p_2}{E}\left(\frac{1 + r_2^2/r_1^2}{r_2^2/r_1^2 - 1} + \mu\right)\left(\frac{r_2^2}{r_1^2}\right)$$

where Δr_2 = change in the outer radius r_2

r_1 = inner radius of the float

r_2 = outer radius of the float

p_2 = outside pressure

E = modulus of elasticity for glass = 173×10^6 psi

μ = Poisson's ratio: for glass = 0.244

For pressures of the order of 200 psi percent volume change amounts to about ±0.01%. Error due to pressure effects is estimated to be less than ±0.007% for densities greater than 60 lbs/cu.ft. These corrections were not applied to the density values since compared to these pressure corrections, the temperature corrections are of the order 0.1%. Estimated accuracy in the experimental liquid density values is ±0.01%.

Sample Calculation:

Float No. 22

Weight of the string in air = 0.0089 g

Weight of the float + string + # 12 float in air = 2.70335 g = W_a

Weight of the float + string + #12 float in water = 0.9946g = W_b

Temperature of the water = 25.05C

Length of the string in water = 2 3/4"

Density of water at 25.05 C = 0.997031 g/cc = d_w

Radius of the string = 0.0015"

$\therefore$ Volume of the float = $(W_a - W_b)/d_w$ = 1.70875/0.997031 = 1.713838 = A

Volume of the submerged string = $\pi r^2 \ell = \pi (0.0015)^2 (2.75)$

= 0.000319 cc

Volume of #12 float = $\underline{0.949115 \text{ cc}}$

$\therefore$ Volume of the string + #12 float = 0.949434 = B

Real volume of the density float = A-B = 0.764404 cc

Wt of the wire = 0.008

Wt of #12 float = 2.1900 g

Wt of the wire + #12 float = 2.198 g = C

$\therefore$ Wt of the density float = W_a - C = 0.50535

$\therefore$ Density of the float = $\dfrac{\text{Wt of the float}}{\text{Vol. of the float}}$ = 0.661103 g/cc

$\therefore$ Float density at 25.05 C = 0.661103 g

Rav for sinking = 33.7597 ohms

Rav for rising = 33.7590 ohms

Average resistance = 33.7694 ohms

Corresponding temperature = 179.081 F = 81.712 C

Coefficient of cubical expansion of Pyrex glass = 0.00000975/c

Volume of the float at 81.712 C = 0.764404 [1+0.00000875(81.712 - 25.05)] = 0.764404 [1+0.000555]

$\therefore$ Density of the float at the temperature of measurement

$$= \frac{0.661103}{1.000555}$$

= 0.660737 g/cc

$\therefore$ Final result = @ 179.081 F, Psi = 0.660737 g/cc.

APPENDIX E

LABORATORY DATA

TABLE E-1

LABORATORY DATA FOR PVT BEHAVIOR OF R-502

OBS.	Mass, GMS (M)		Volume,	$\frac{V}{\underline{V}}$	Temperature (T)		Pressure, Psi			
No.	Charged	Recovered	h, cms	Cuft/lb.	Rt, Ohms	R	Gauge	Bar.	Corr.	Absolute
F1	32.716	32.715	97.73	0.58242	28.2870	541.14	67.12	14.41	+0.42	81.95
F2			69.72	0.46624	28.2866	541.13	84.65	14.41	+0.56	99.62
F3			54.04	0.40438	28.2869	541.14	105.0	14.39	-2.45	116.94
F4			30.80	0.30714	28.2869	541.14	129.8	14.39	-2.90	141.29
F5			16.76	0.24841	28.2872	541.14	155.2	14.40	-3.37	166.23
F6			9.16	0.21655	28.2865	541.13	168.0	14.40	-3.60	178.80
F7	27.010	26.995	70.25	0.57766	33.7513	639.50	85.15	14.30	+0.58	100.93
F8			47.88	0.46102	33.7513	639.50	111.80	14.30	-2.57	123.53
F9			25.685	0.34530	33.7516	639.50	149.5	14.30	-3.27	160.53
F10			13.10	0.27968	33.7515	639.50	183.0	14.30	-3.87	193.43
F11			2.645	0.22516	33.7534	639.53	222.7	14.30	-4.57	232.43
F12	54.210	54.201	97.565	0.35877	33.7594	639.64	143.0	14.34	-3.15	154.19
F13			70.160	0.28757	33.7583	639.62	178.0	14.34	-3.80	188.54
F14			25.72	0.17213	33.7575	639.61	279.7	14.34	-5.55	288.49
F15			13.10	0.13934	33.7577	639.61	330.3	14.34	-6.40	338.24

TABLE E-1 (contd.)

Obs.	Mass, GMS (M)		Volume, $\underline{V}$		Temperature (T)		Pressure, Psi.			
No.	Charged	Recovered	h, cms	$\underline{V}$ Cuft/lb.	Rt, Ohms	R	Gauge	Bar.	Corr.	Absolute
F16			2.375	0.11148	33.7588	639.63	386.5	14.34	-7.35	393.49
F17	355.92	355.81	97.44	0.05460	33.7566	639.59	547.0	14.26	-5.9	555.36
F18			83.50	0.04909	33.7569	639.60	561.0	14.26	-6.0	569.26
F19			74.035	0.04534	33.7573	639.60	568.0	14.26	-6.0	576.26
F20			66.105	0.04220	33.7572	639.60	573.5	14.26	-6.0	581.76
F21			54.875	0.03776	33.7580	639.62	578.0	14.26	-6.0	586.26
F22			18.03	0.02318	33.7555	639.57	582.0	14.26	-6.0	590.28
F23			13.455	0.02137	33.7572	639.60	595.0	14.26	-6.0	603.26
F24			9.695	0.01988	33.7552	639.57	626.0	14.26	-6.0	634.26
F25			5.695	0.01830	33.7569	639.60	722.0	14.26	-6.65	729.61
F26	487.20	487.04	89.405	0.03756	33.7561	639.58	578.5	14.27	-6.0	586.77
F27			38.40	0.02282	33.7536	639.54	586.0	14.27	-6.0	594.27
F28			29.925	0.02037	33.7548	639.56	616.0	14.27	-6.0	624.27
F29			20.635	0.01768	33.7534	639.53	800.0	14.27	-7.8	806.47
F30			18.21	0.01698	33.7548	639.56	924.0	14.27	-8.0	930.27

TABLE E-1 (contd.)

Obs. No.	Mass, GMS (M) Charged	Recovered	Volume, V h, cms	$\underline{V}$ Cuft/lb.	Temperature (T) Rt, Ohms	R	Pressure, Psi. Gauge	Bar.	Corr.	Absolute
F31			16.305	0.01643	33.7542	639.55	1062.0	14.27	-8.0	1068.27
F32			14.675	0.01596	33.7548	639.56	1219.0	14.27	-9.0	1224.27
F33			13.11	0.01551	33.7536	639.54	1414.0	14.27	-10.0	1418.29
F34			11.975	0.01518	33.7556	639.57	1599.0	14.29	-11.0	1602.29
F35			10.765	0.01483	33.7558	639.58	1837.0	14.29	-13.5	1837.79
F36			10.165	0.01466	33.7560	639.58	1976.0	14.29	-15.0	1975.29
F37	512.78	512.78	97.965	0.03761	35.1023	664.06	701.0	14.24	-7.5	707.74
F38			65.885	0.02891	35.1012	664.04	745.0	14.24	-7.5	751.74
F39			51.66	0.02506	35.1014	664.05	776.0	14.24	-7.7	782.54
F40			41.405	0.02228	35.1010	664.04	828.0	14.24	-8.2	834.04
F41			34.40	0.02038	35.1006	664.03	904.0	14.24	-8.2	909.74
F42			28.33	0.01873	35.1003	664.03	1046.0	14.24	-8.6	1051.64
F43			22.10	0.01705	35.1012	664.04	1364.0	14.32	-11.5	1366.82
F44			19.145	0.01624	35.1020	664.06	1650.0	14.32	-14.10	1650.22

TABLE E-1 (contd.)

Obs. No.	Mass, GMS (M)		Volume, V		Temperature (T)		Pressure, Psi.			
	Charged	Recovered	h, cms	$\underline{V}$ Cuft/lb.	Rt, Ohms	R	Gauge	Bar.	Corr.	Absolute
F45			16.875	0.01563	35.1015	664.05	1965.0	14.32	-17.0	1962.32
F46	177.32	177.30	97.985	0.10894	35.2170	666.15	427.5	14.45	-8.55	433.40
F47			69.455	0.08640	35.2160	666.14	498.2	14.46	-9.50	503.16
F48			41.050	0.06397	35.2162	666.14	585.0	14.46	-6.0	593.46
F49			15.13	0.04350	35.2166	666.15	682.0	14.46	-7.2	689.26
F50			2.83	0.03378	35.2162	666.14	730.0	14.46	-7.5	736.96
F51	117.32	177.30	97.67	0.10740	37.5584	708.99	483.5	14.51	-9.3	488.71
F52			72.855	0.08796	37.5570	708.96	555.0	14.51	-6.0	563.51
F53			51.28	0.07105	37.5573	708.97	641.0	14.51	-6.5	649.01
F54			31.665	0.05568	37.5571	708.97	745.0	14.51	-7.5	752.01
F55			12.765	0.04088	37.5610	709.04	876.5	14.51	-8.5	882.51
F56			2.93	0.03317	37.5565	708.95	971.0	14.51	-8.5	977.00
F57	497.3	497.3	99.035	0.03876	37.7497	712.50	919.0	14.10	-8.5	924.60
F58			75.24	0.03210	37.7517	712.54	1011.0	14.10	-8.5	1016.60

TABLE E-1 (contd.)

Obs.	Mass, GMS (M)		Volume,	$\underline{V}$	Temperature (T)		Pressure, Psi.			
No.	Charged	Recovered	h, cms	$\underline{V}$ Cuft/1b.	Rt, Ohms	R	Gauge	Bar.	Corr.	Absolute
F59			53.625	0.02605	37.7529	712.56	1147.0	14.10	-9.5	1151.60
F60			42.16	0.02285	37.7536	712.57	1286.0	14.10	-10.8	1289.30
F61			34.935	0.02083	37.7540	712.58	1444.0	14.10	-12.2	1445.90
F62			30.135	0.01948	37.7536	712.57	1613.0	14.10	-13.8	1613.30
F63			27.25	0.01868	37.7543	712.59	1760.0	14.10	-15.1	1759.00
F64			24.36	0.01787	37.7556	712.61	1959.0	14.10	-16.9	1956.20

TABLE E-2

Laboratory Data for Volume, Calibrations with Carbon Dioxide

Obs. No.	Mass GMS (M)		Height (h) CMS	Temperature (T)		Pressure Psi.			Absolute	$Z=\frac{PV}{RT}$	Vol. (V) $= in^3$
	Charged	Recovered		Rt, Ohms	R	Gauge	Bar.	Corr.			
C1	12.1632	12.1573	96.95	28.2818	541.05	67.40	14.31	+0.42	82.13	0.971819	72.81
C2			71.10	28.2836	541.08	84.85	14.31	+0.54	99.70	0.965732	59.22
C3			53.94	28.2842	541.09	104.8	14.31	-2.45	116.66	0.959725	50.30
C4			33.27	28.2841	541.09	135.3	14.31	-3.0	146.61	0.949069	39.58
C5			20.42	28.2838	541.08	163.5	14.31	-3.52	174.29	0.937463	32.88
C6			10.065	28.2837	541.08	195.5	14.31	-4.10	205.71	0.924197	27.47
C7			2.11	28.2839	541.09	229.0	14.31	-4.67	238.64	0.910324	23.32
C8			96.95	28.2841	541.09	67.40	14.31	+0.42	82.13	0.971819	72.82
C9	21.2381	21.2341	97.755	28.2843	541.10	127.3	14.31	-2.86	138.75	0.951865	73.24
C10			71.985	28.2840	541.09	156.7	14.31	-3.41	165.60	0.940252	59.89
C11			54.015	28.2841	541.09	186.3	14.31	-3.96	196.66	0.928009	50.38
C12			33.210	28.2833	541.07	236.0	14.31	-4.81	245.50	0.907434	39.46
C13			20.420	28.2838	541.08	280.3	14.31	-5.56	289.05	0.889088	32.84

TABLE E-2 (contd.)

Obs. No.	Mass GMS (M)		Height (h) CMS	Temperature (T)		Pressure Psi.					Vol. (V) $= in^3$
	Charged	Recovered		Rt, Ohms	R	Gauge	Bar.	Corr.	Absolute	$Z=\frac{P\bar{V}}{RT}$	
C14			10.065	28.2835	541.08	329.8	14.31	-6.40	337.71	0.868588	27.46
C15			2.045	28.2835	541.08	381.0	14.31	-7.25	388.06	0.847377	23.31
C16			97.755	28.2843	541.10	127.3	14.31	-2.86	138.75	0.951865	73.24
C17	34.0142	33.9802	97.70	33.7589	639.63	248.5	14.33	-5.02	257.81	0.948715	74.29
C18			66.35	33.7587	639.63	321.3	14.33	-6.25	329.38	0.934029	57.25
C19			41.40	33.7589	639.63	413.0	14.33	-7.77	419.56	0.915524	44.05
C20			25.945	33.7588	639.63	499.0	14.33	-5.40	507.93	0.897391	35.67
C21			13.45	33.7596	639.64	602.0	14.33	-6.00	610.33	0.876066	28.98
C22			2.335	33.7599	639.65	635.0	14.33	-6.80	742.53	0.847085	23.03
C23			97.70	33.7594	639.64	248.5	14.33	-5.02	257.81	0.948715	74.29
C24	79.993	79.991	97.655	33.7601	639.65	558.5	14.28	-6.00	566.78	0.885324	74.25
C25			66.605	33.7601	639.65	700.0	14.28	-6.40	707.88	0.854690	57.39
C26			41.760	33.7615	639.68	874.0	14.28	-8.00	880.28	0.816896	44.11
C27			26.00	33.7600	639.65	1033.5	14.28	-8.00	1039.78	0.781645	35.73

TABLE E-2 (contd.)

Obs. No.	Mass GMS (M)		Height (h) CMS	Temperature (T)		Pressure Psi.				$Z=\frac{PV}{RT}$	Vol. (V) = in^3
	Charged	Recovered		Rt, Ohms	R	Gauge	Bar.	Corr.	Absolute		
C28			13.445	33.7611	639.67	1207.0	14.28	-9.0	1212.78	0.739150	28.98
C29			2.32	33.7604	639.66	1415.0	14.28	-10.0	1419.28	0.687911	23.04
C30			97.655	33.7616	639.70	561.0	14.28	-6.0	569.28	0.885324	73.93
C31	80.032	80.276	96.315	35.0994	664.01	600.0	14.41	-6.0	608.41	0.893310	72.61
C32			73.590	35.0990	664.00	708.0	14.41	-7.5	714.91	0.973840	60.45
C33			57.00	35.0988	664.00	812.0	14.41	-8.1	818.31	0.854930	51.67
C34			40.760	35.0984	664.00	946.0	14.41	-8.5	951.91	0.830506	43.15
C35			27.550	35.0992	664.01	1092.0	14.41	-9.0	1097.41	0.803069	36.19
C36			13.315	35.0994	664.01	1310.0	14.41	-11.0	1313.40	0.760943	28.65
C37			3.185	35.0998	664.02	1528.0	14.41	-13.0	1529.40	0.718820	23.24
C38			1.235	35.0985	664.00	1578.0	14.41	-13.4	1579.00	0.709140	22.21
C39			96.315	35.0998	664.02	600.0	14.41	-6.0	608.41	0.893310	72.61
C40	23.0279	23.0279	97.455	35.2143	666.10	178.3	14.50	-4.3	188.50	0.968075	73.18
C41			75.00	35.2158	666.13	214.0	14.50	-5.1	223.40	0.462013	61.36

TABLE E-2 (contd.)

Obs. No.	Mass GMS (M)		Height (h) CMS	Temperature (T)		Pressure Psi.			Absol- ute	$Z=\frac{P\underline{V}}{RT}$	Vol. ($\underline{V}$) = in^3
	Charged	Recovered		Rt, Ohms	R	Gauge	Bar.	Corr.			
C42			51.80	35.2151	666.12	269.0	14.50	-6.1	2.77.40	0.952564	48.93
C43			31.60	35.2159	666.13	344.0	14.50	-7.3	351.20	0.939687	38.13
C44			15.39	35.2148	666.11	440.3	14.50	-8.75	446.05	0.923138	29.49
C45			2.91	35.2158	666.13	554.0	14.50	-6.00	562.50	0.902819	22.87
C46			97.455	35.2160	666.13	178.3	14.50	-4.30	188.50	0.968075	73.18
C47	23.0279	23.0279	98.855	37.5542	708.91	191.5	14.50	-4.6	201.40	0.972955	73.26
C48			72.860	37.5558	708.94	237.8	14.50	-5.55	246.75	0.966754	59.42
C49			49.00	37.5546	708.92	303.0	14.50	-6.65	310.85	0.957990	46.74
C50			26.92	37.5556	708.94	402.0	14.50	-8.20	408.30	0.944665	35.09
C51			13.70	37.5558	708.94	498.2	14.50	-9.50	503.20	0.931690	28.08
C52			2.785	37.5562	708.95	614.0	14.50	-6.10	622.40	0.915401	22.31
C53			98.855	37.5555	708.94	191.5	14.50	-4.60	201.40	0.972955	73.26
C54	73.5150	73.4840	98.86	37.6911	711.43	601.0	14.20	-6.0	609.2	0.918411	73.23
C55			74.925	37.6907	711.42	717.0	14.20	-7.5	723.7	0.903063	60.61

TABLE E-2 (contd.)

Obs. No.	Mass GMS (M)		Height (h) CMS	Temperature (T)		Pressure Psi.			Absol- ute	$Z=\frac{PV}{RT}$	Vol. (V) $=in^3$
	Charged	Recovered		Rt, Ohms	R	Gauge	Bar.	Corr.			
C56			57.84	37.6920	711.44	830.0	14.20	-8.2	836.01	0.888009	51.60
C57			43.015	37.6906	711.42	962.0	14.20	-8.5	967.71	0.870355	43.69
C58			29.090	37.6926	711.45	1129.0	14.20	-8.5	1134.72	0.848051	36.30
C59			16.00	37.6929	711.45	1350.0	14.20	-11.4	1352.83	0.818987	29.41
C60			2.680	37.6925	711.45	1686.0	14.20	-14.4	1685.84	0.774611	22.32
C61			98.86	37.6931	711.46	601.0	14.20	-6.0	609.2	0.917736	73.23

TABLE E-3

Laboratory Data for Low Vapor Pressure Measurements with R-502

Obs. No.	Height of Mercury in the Legs of Manometer h_1 cm	h_2 cm	Barometric Pressure mmHg	Resistance of the Therm. - Ohms	Temp. R	Vapor Pressure mmHg	psia
1	58.205	60.273		14.9870	308.55	20.68	0.3999
2	94.050	26.045	736.80	16.228	329.79	56.75	1.0974
3	92.612	27.784	736.80	16.880	340.99	88.520	1.7117
4	92.470	27.681	736.80	16.960	342.53	88.910	1.7192
5	86.462	24.892	734.20	17.4304	350.02	118.60	2.2963
6	88.151	26.414	736.70	17.4340	350.07	119.33	2.3074
7	89.129	27.404	737.70	17.4384	350.16	120.45	2.3291
8	90.526	29.491	736.80	17.431	350.48	126.45	2.4451
9	90.861	29.684	736.80	17.451	350.84	124.03	2.3984
10	87.539	29.055	737.80	17.7907	356.22	152.96	2.9578
11	85.121	29.444	736.80	18.1046	361.64	180.03	3.4812
12	83.402	28.230	733.90	18.1430	362.30	182.18	3.5228
13	82.631	33.936	737.80	18.6337	370.78	250.85	4.8507
14	79.738	31.746	733.90	18.7194	371.18	253.98	4.9112

Table E-3 (contd.)

Obs. No.	Height of Mercury in the Legs of Manometer		Parametric Pressure mmHg	Resistance of the Therm.-Ohms	Temp. R	Vapor Pressure	
	h_1 cm	h_2 cm				mmHg	Psia
15	75.620	35.666	733.20	19.2368	381.22	333.66	6.4520
16	76.485	38.425	736.90	19.3235	382.72	356.30	6.8898
17	73.709	42.966	737.80	19.6845	388.10	430.37	8.3221
18	71.503	43.873	737.40	19.8559	391.96	461.10	8.9163
19	68.508	43.429	733.70	19.9644	393.85	482.91	9.3380
20	63.242	51.800	737.40	20.4740	402.71	622.98	11.860
21	60.520	50.780	733.70	10.5753	404.48	636.30	12.304
22	59.108	52.444	733.80	20.5950	404.82	667.16	12.901
23	57.540	57.540	727.70	20.8900	409.96	737.70	14.265
24	52.000	64.710	737.80	21.2735	416.65	864.90	16.725

TABLE E-4

Laboratory Data for High Vapor Pressure Measurements with R-502

Mass of The Sample	Observed Pressure psig	Barometric Pressure mmHg	Calibration Correction	Thermometer Resistance Ohms	Average Temperature T(R)	Average Pressure P (psia)
144.231	210.7	739.5	-0.62	29.2370	558.13	224.38
	210.7	739.5	-0.62	29.2388		
	210.7	739.5	-0.62	29.2387		
478.126	212.8	739.2	-0.62	29.2391	558.15	226.53
	212.8	739.2	-0.62	29.2368		
	212.8	739.2	-0.62	29.2395		
79.7195	211.6	743.1	-0.62	29.2414	558.25	225.35
	211.6	743.1	-0.62	29.2422		
151.203	218.3	746.2	-0.68	29.3521	560.19	232.05
	218.3	746.2	-0.68	29.3516		
	218.3	746.2	-0.68	29.3528		
144.231	219.5	736.4	-0.68	29.3530	560.21	233.06
	219.5	736.4	-0.68	29.3519		
	219.5	736.4	-0.68	29.3523		
84.0854	227.8	741.2	-0.83	29.4745	562.38	240.78
	227.9	739.7	-0.83	29.4744		

TABLE E-4 (contd.)

Mass of The Sample	Observed Pressure psig	Barometric Pressure mmHg	Calibration Correction	Thermometer Resistance Ohms	Average Temperature T(R)	Average Pressure P (psia)
478.126	253.4	738.0	-1.10	29.9292	570.52	266.63
	253.5	738.0	-1.10	29.9288		
	253.4	738.0	-1.10	29.9285		
478.126	290.0	738.0	-1.46	30.4928	580.65	302.77
	290.0	738.0	-1.46	30.4923		
	290.0	738.0	-1.46	30.4929		
79.7195	322.4	741.2	-1.65	30.9980	589.71	335.08
	322.4	741.2	-1.65	30.9992		
144.231	324.0	737.0	-1.65	30.9981	589.72	336.62
	324.0	737.5	-1.65	30.9993		
	324.0	737.3	-1.65	30.9990		
478.126	327.0	737.7	-1.68	31.0135	590.00	339.63
	327.0	737.7	-1.68	31.0138		
	327.0	737.7	-1.68	31.0128		
151.203	402.0	738.8	-1.50	31.9517	606.93	414.9
	402.0	738.8	-1.50	31.9515		
	402.0	738.8	-1.50	31.9515		
478.126	411.7	736.5	-1.80	32.0609	608.89	424.20
	411.9	736.5	-1.80	32.0606		
	411.7	736.5	-1.80	32.0603		
	411.6	736.5	-1.80	32.0607		

TABLE E-4 (contd.)

Mass of The Sample	Observed Pressure psig	Barometric Pressure mmHg	Calibration Correction	Thermometer Resistance Ohms	Average Temperature T(R)	Average Pressure P (Psia)
79.7195	420.5	744.7	-1.80	32.1273	610.05	433.1
	420.5	744.7	-1.80	32.1269		
	420.5	744.7	-1.80	32.1266		
84.0854	417.3	746.8	-1.80	32.1289	610.09	430.3
	417.7	746.8	-1.80	32.1295		
	418.0	746.8	-1.80	32.1287		
151.203	424.4	737.5	-1.80	32.2370	612.08	436.86
	424.4	737.5	-1.80	32.2365		
	424.4	737.5	-1.80	32.2374		
144.231	423.0	742.1	-1.80	32.2421	612.17	435.55
	423.0	742.1	-1.80	32.2416		
	423.0	742.1	-1.80	32.2418		
478.126	484.5	736.7	-2.12	32.8390	622.94	497.11
	485.0	736.7	-2.12	32.8373		
	485.0	736.7	-2.12	32.8374		
144.231	488.0	737.5	-2.32	32.9168	624.33	499.94
	488.0	737.5	-2.32	32.9160		
	488.0	737.5	-2.32	32.9163		
478.126	514.5	736.6	-2.35	33.1825	629.22	527.45
	515.5	736.6	-2.35	33.1841		

TABLE E-4 (contd.)

Mass of The Sample	Observed Pressure psig	Barometric Pressure mmHg	Calibration Correction psi	Thermometer Resistance Ohms	Average Temperature T(R)	Average Pressure P (psia)
151.203	577.5	736.4	-3.0	33.7417	639.32	588.8
	577.5	736.4	-3.0	33.7416		
	577.5	736.4	-3.0	33.7408		
478.126	578.0	738.6	-3.0	33.7465	639.41	589.34
	578.0	738.6	-3.0	33.7470	639.42	589.34

TABLE E-5

Laboratory Data for Saturated Liquid Density Measurements with R-502

Float No.	Weight of Wire g	Weight of Float +wire+ (Float #12*) in Air g	Weight of Float +wire +(Float #12*) in Water g	Length of Wire in Water (in.)	Temp. of Water C	Density of Float g/cc
22	0.0080	2.70335	0.9946	2.75	25.05	0.661103
14	0.010524	2.8461	1.0292	5.5	20.5	0.741526
20	0.00655	3.1684	1.0618	2.3	18.55	0.837323
16	0.10017	2.79595	1.2001	5.0	20.2	0.918109
5	0.0075	0.8552	0.0869	2.5	20.2	1.101730
18	0.0075	1.1539	0.1560	2.5	20.8	1.146829
6	0.0075	1.3118	0.2681	2.5	20.45	1.248425
8	0.0075	1.0418	0.2155	2.5	20.8	1.249702
2	0.0075	1.4373	0.3021	2.5	20.6	1.25740
1	0.0075	1.2224	0.2721	2.5	20.7	1.27634
4	0.0075	1.2538	0.3127	2.5	20.4	1.32222
3	0.0075	1.4943	0.5120	2.5	20.6	1.511179
7	0.0075	1.6163	0.6529	2.5	20.3	1.66731

TABLE E-5 (contd.)

Float Sinking Ohms	Float Rising Ohms	Average Ohms	Temp. R**	Saturated Liquid Density Corrected for the Expansion g/cc	lbs/cuft
33.5797	33.7590	33.7593	638.75	0.660737	41.25
33.6022	33.6010	33.6016	635.89	0.741095	46.27
33.1918	33.1893	33.1905	628.45	0.836854	52.24
32.5874	32.5845	32.5860	617.53	0.917660	57.29
30.2764	30.2716	30.2740	575.92	1.101446	68.76
29.4812	29.4772	29.4792	561.68	1.146630	71.58
27.3976	27.3913	27.3945	524.50	1.248425	77.94
27.3375	27.3341	27.3358	523.46	1.249702	78.02
27.1396	27.1341	27.1368	519.92	1.257400	78.50
26.5944	26.5867	26.5905	510.22	1.27634	79.68
25.5440	25.5366	25.5403	491.67	1.33247	82.56
19.8812	19.8750	19.8781	392.35	1.152295	94.41
14.3868	14.3770	14.3819	297.87	1.66939	104.22

+About 0.1 Ohm _1C
*Float #12 is used when neede
**R = F+459.67

TABLE E-6

Laboratory Data for Critical Temperature Measurements with R-502

Obs. No.	Observation	N	R	Mean	Temperature T_c R
1	Liquid meniscus just appeared	33.7465	33.7440	33.7453	639.3861
2	Liquid meniscus just disappeared	33.7487	33.7461	33.7474	639.4241
3	Liquid meniscus just appeared	33.7468	33.7440	33.7454	639.3879

Average T_c = 639.40 R

T_c = 639.72 - Measured by Hossain

Critical temperature of R-502 = 639.56 R

APPENDIX F

THE EQUATION OF STATE

History of the development of the following equation of state goes back to the work of Martin and Hou (91). Improvement to the original equation was made by Martin and Hou (92). The most recent work is published by Martin (89). Bhada (15) used the same equation to correlate his data on PVT behavior of carbon tetrafluoride. The following analysis is in continuation of the previous development work. For this development we used the PVT data on R-22 since it is available accurately over an extensive range.

The following equation was found to have the best characteristics:

$$P = \frac{RT}{V-b} + \frac{A_2 + B_2T + C_2\,e^{-kt}}{(V-b)^2} + \frac{A_3 + B_3T + C_3\,e^{-kT}}{(V-b)^3} + \frac{A_4 + B_4T + C_4\,e^{-kT}}{(V-b)^2}$$

$$+ \frac{A_5 + B_5T}{e^{a_1V}(1+c_1e^{a_1V})} + \frac{A_6B_6T}{e^{a_2V}(1+c_2e^{a_2V})} \qquad \text{(F-1)}$$

Equation (F-1) contains the following 19 constants.

A_2
B_2
C_2
A_3
B_3
C_3
A_4
B_4
C_4
A_5
B_5
A_6
B_6
k
b
a_1
c_1
a_2
c_2
Total = 19

At first it may seem like a formidable task to evaluate these nineteen constants. But by choosing a few generalized conditions, we need only a few boundary conditions. Complete mechanics of the data fitting is described below.

Basis of Equation (F-1) is the fourth degree virial equation.

$$P = \frac{RT}{V} + \frac{f_2}{V^2} + \frac{f_3}{V^3} + \frac{f_4}{V^4} \qquad \text{(F-2)}$$

where $f_i = A_i + B_i\ T{+}C_i e^{-kT}$ (Assumed)

The first step in evaluating constants is to fit Equation (F-2) at the critical isotherm where Equation (F-3) can be written as follows:

$$P = \frac{RT_c}{V} + \frac{f_2(T_c)}{V^2} + \frac{f_3(T_c)}{V^3} + \frac{f_4(T_c)}{V^4} \qquad \text{(F-3)}$$

There are three unknowns in Equation (F-3) namely, $f_2(T_c)$, $f_3(T_c)$ and $f_4(T_c)$ which can be evaluated by using the following well-known derivative conditions at the critical point.

$$\left(\frac{dp}{dV}\right)_{T_c} = \left(\frac{d^2p}{dV^2}\right)_{T_c} = \left(\frac{d^3p}{dV^3}\right)_{T_c} = 0 \text{ at } V = V_c \qquad \text{(F-4)}$$

The result is as follows:

$$f_2(T_c) = -3R^2T_c^2/8P_c \qquad \text{(F-5)}$$

$$f_3(T_c) = R^3T_c^3/16P_c^{\ 2} \qquad \text{(F-6)}$$

$$f_4(T_c) = -R^4T_c^{\ 4}/256P_c^{\ 3} \tag{F-7}$$

Then Equation (F-2) can be written as:

$$P = \frac{RT}{V} - \frac{3R^2T_c^{\ 2}}{8P_cV^2} + \frac{R^3T_c^{\ 3}}{16P_c^{\ 2}V^3} - \frac{R^4T_c^{\ 4}}{256P_c^{\ 3}V^4} \tag{F-8}$$

Equation (F-8) predicts the generalized second virial coefficient at the critical temperature of -0.375 and the critical compressibility factor of 0.250. For R-22 the generalized second virial coefficient at the critical temperature is around -0.345 and the critical compressibility factor is 0.2667. Therefore, Equation (F-8) is not expected to do well on the critical isotherm. As elaborated by Martin, we need a translational term on the volume axis which shall be termed "b". Equation (F-8) can now be written:

$$P = \frac{RT}{V-b} - \frac{3R^2T_c^{\ 2}}{8P_c(V-b)^2} + \frac{R^3T_c^{\ 3}}{16P_c(V-b)^3} - \frac{R^4T_c^{\ 4}}{256P_c^{\ 3}(V-b)^4} \tag{F-9}$$

By linearly translating the volume, we do not upset the derivative conditions of Equation (F-4) which is a consequence of differential calculus. In this case we obtain the following relations for the generalized second virial coefficient at the critical temperature and the critical compressibility factor.

$$\frac{BP_c}{RT_c} = -\frac{3}{8} + \frac{bP_c}{RT_c} \tag{F-10}$$

and

$$\frac{P_c V_c}{RT_c} = \frac{1}{4} + \frac{bP_c}{RT_c} \tag{F-11}$$

At this point we can work with the actual critical isotherm data.

In order to obtain points in the critical isotherm, we used PVT data of R-22 reported by Michels (99) and Zander (140). This data is plotted as isometrics in Fig. V-1. Analysis of this information gave us points up to 2 times the critical density (ρ_c). There were no points between the region of critical density and 1.3 times the critical density. To fill this region an interpolation technique was used. A semilog plot of (P_R-1) vs. (ρ_R-1), is linear in the region of P_c to 1.3 P_c (Fig. F-1). Through the experimental data around 1.3ρ_c, a straight line AB (Fig. F-1) was drawn. The same straight line was then translated five times toward ρ_c to obtain synthetic values of P_R vs. ρ_R.

To extend the data beyond 2.4 ρ_c we used the critical isotherm of CO_2 (89). Carbon dioxide has a value of Z_c = 0.274 which is very close to the critical compressibility factor of R-22. A semilog plot was made of P_R vs. ρ_R for carbon dioxide and R-22 (Fig. F-2). Using interpolation techniques on Zander's (140) isometric data, the last point on the critical isotherm of R-22 was at about 2 ρ_c. The critical isotherm of carbon dioxide goes to 2.52 ρ_c. The overlap of R-22 data and carbon dioxide data up to 2 ρ_c is excellent as shown in Fig. F-2. Hence by following the critical isotherm of carbon dioxide, synthetic points for R-22 were evaluated up to 2.6 ρ_c. All these critical isotherm values are tabulated in Table F-1.

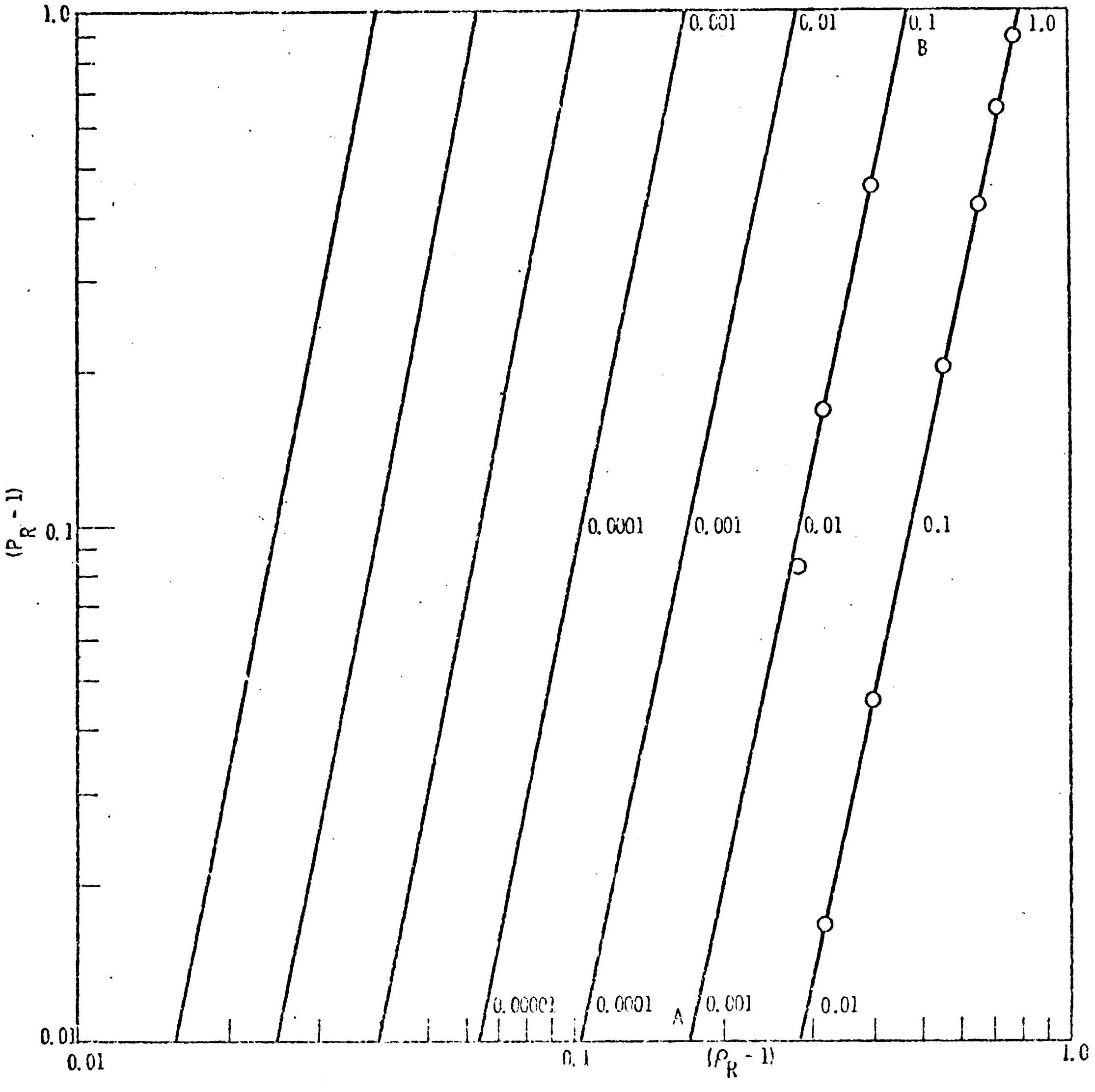

Fig. F.1 Plot of $(P_R - 1)$ vs $(\rho_R - 1)$ for R-22 at the critical temperature

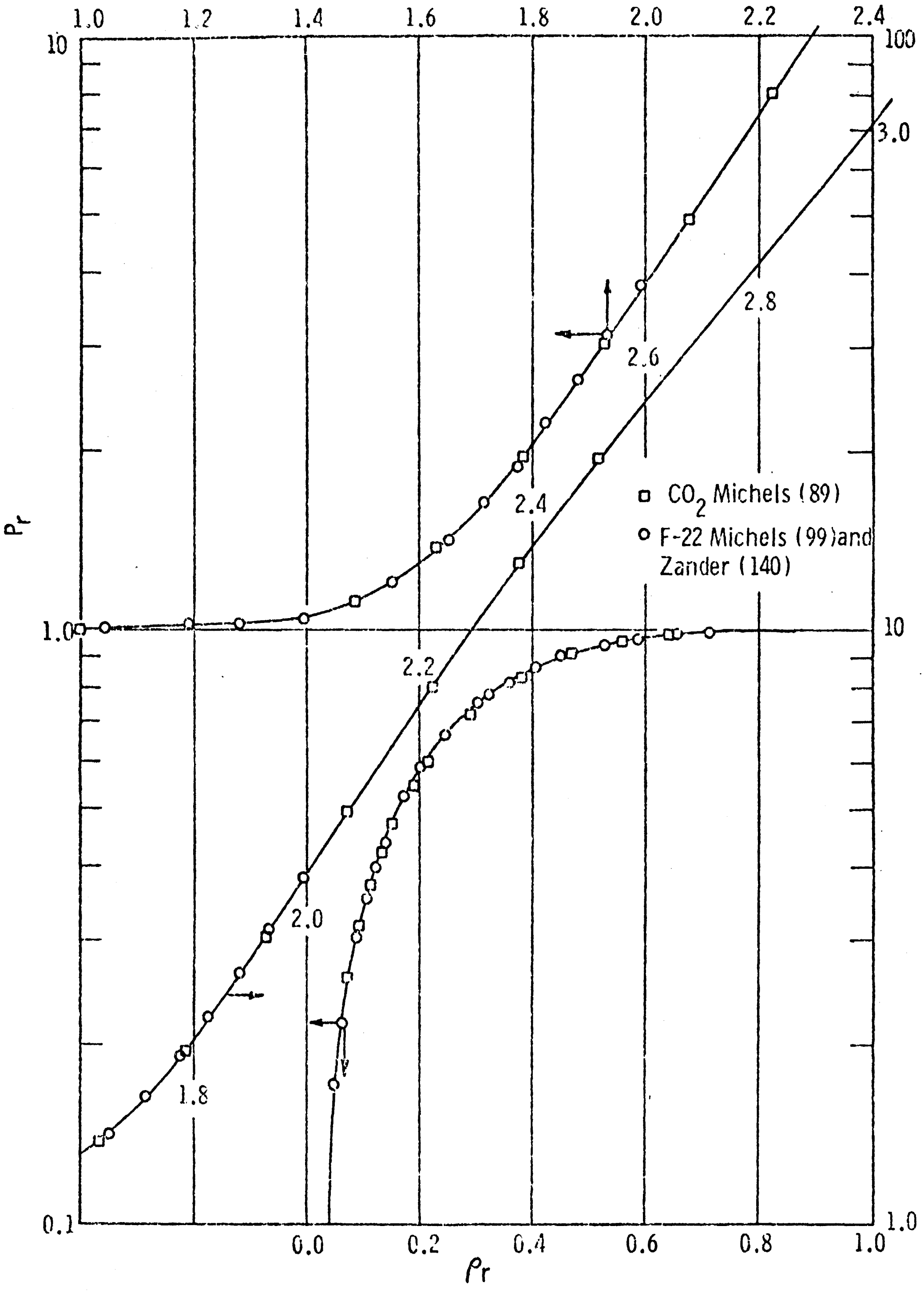

Fig. F.2. Plot of P_r vs ρ_r from R-22 and Carbon Dioxide at the Critical Temperature

Using the critical isotherm of R-22, we found out that the best fit is obtained if we choose $bP_c/RT_c = 0.029$ in Equation (F-10), giving the generalized second virial coefficient at the critical temperature of R-22 to be -0.346. The corresponding critical compressibility factor is 0.279. Equation (F-9), with the selected value of b, fits the critical isotherm data very well up to the critical density but beyond that it deviates from the experimental data.

At this stage to evaluate additional terms to Equation (F-9), a semilog plot of residual reduced pressure ΔP_R vs. reduced volume V_R is made, as elaborated by Martin (89) and Bhada (15). The residual term ΔP_R is defined by the following equation:

$$\begin{aligned}\Delta P_R &= P_{R_{exp}} - P_{R_{cal}} \\ &= P_{R_{exp}} - \frac{1}{P_c}\left(\frac{RT_c}{V-b} - \frac{3R^2T_c^{\,2}}{8P_c(V-b)^2} + \frac{R^3T_c^{\,3}}{16P_c^{\,2}(V-b)^3}\right. \\ &\quad \left. - \frac{R^4T_c^{\,4}}{256P_c^3\,(V-b)^4}\right) \qquad \text{(F-12)}\end{aligned}$$

Such a plot of ΔP_R vs. V_R for R-22 is presented in Fig. F-3. Through most of the points in Fig. F-3, a straight line can be drawn up to 2.4 ρ_c, thereby indicating that only one term of the form $f_5(T_c)/e^{aV}(1+ce^{aV})$ would suffice. In this term the multiplying term $(1+ce^{aV})$ is a damping factor to take into account that the plot in Fig. F-3 is nonlinear and extremely steep near the critical density. Our investigation showed that if only one term is used, it does not give us enough freedom to obtain good temperature variations of PVT data in the compressed vapor

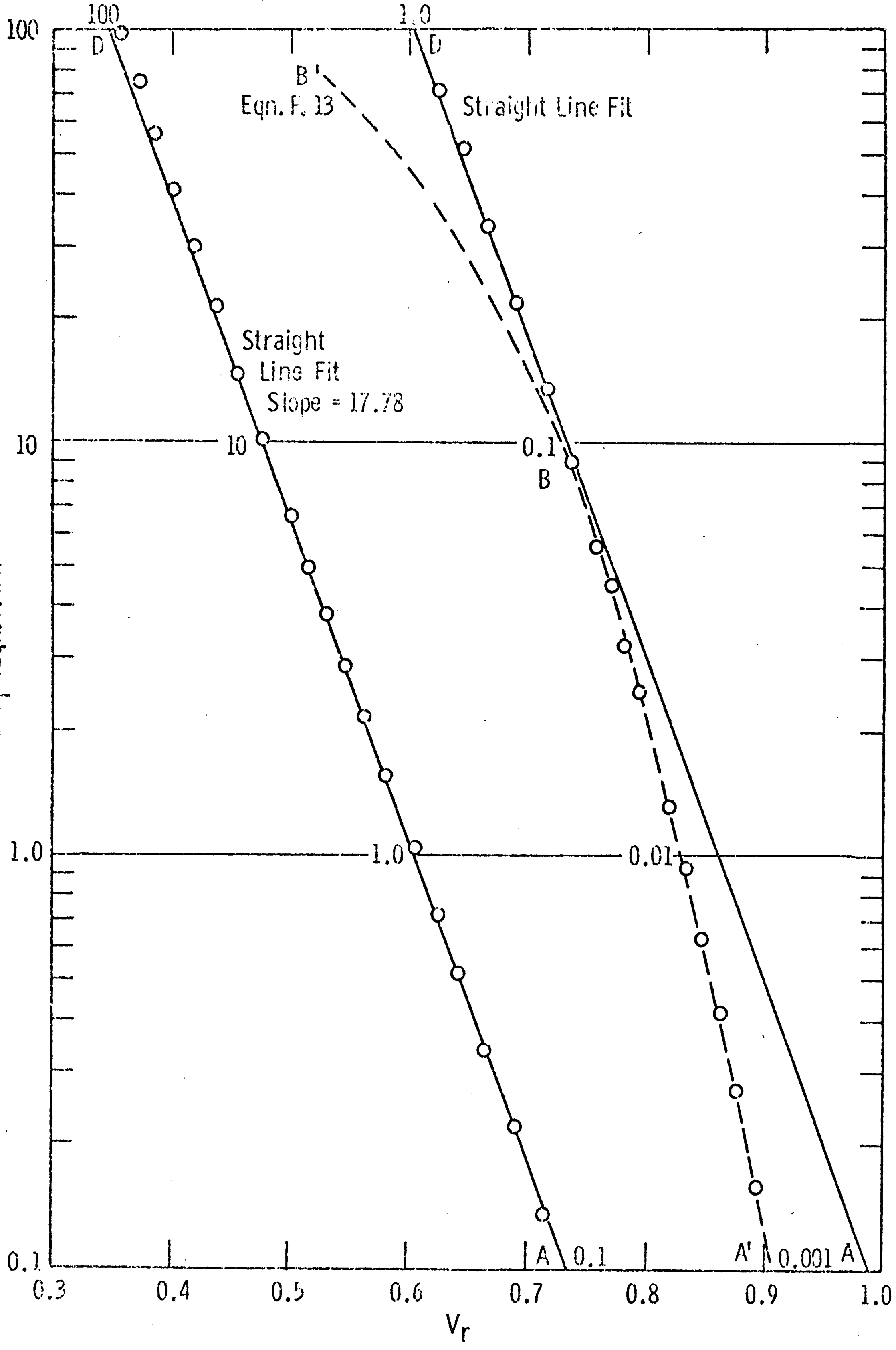

Fig. F. 3. Plot of ΔP_r (Eqn. F. 12) vs V_r for Chlorodifluoromethane (R-22) at the Critical Temperature region. Further investigation showed that one exponential term must span a distance of about 0.4 ρ_c. Making our objective as to fit the PVT data up to 1.8 ρ_c as best as we can, we selected two exponential terms as shown in Equation (F-1).

The method of evaluating the two exponential terms in Equation (F-1) is slightly different from the one used before (15). With respect to Fig. F-3, line AD has a slope of about 17.779. For the fifth term, $f_5(T_c)/e^{a_1V}(1+c_1e^{a_1V})$ to account only up to 1.4 ρ_c, a_1 is selected less than the slope of line AD(17.779). Then the two unknowns $f_5(T_c)$ and c_1 can be determined from the experimental data points. The calculations are as follows:

Let $a_1 = 16.0$

$$\ln \Delta P_R = \ln f_5(T_c) - a_1V_R - \ln\,(1+c_1e^{a_1V_R}) \tag{F-13}$$

The data is given in the following table.

TABLE F-2

Values of P_R and V_R to Evaluate c_1 and $\ln f_5(T_c)$

No.	V_R	P_R	a_1V_R	$\ln\Delta P_R$	$(\ln\Delta P_R)$calc
1	0.9601	0.0005	15.3616	-7.6009	-7.514
2	0.7805	0.0321	12.4880	-3.4389	-3.439
3	0.7594	0.0534	12.1504	-2.9299	-2.9529
4	0.7150	0.1327	11.440	-2.0197	-2.0197

Equation (F-13) can be solved for two values of P_R and V_R. Here we have a choice of several pairs of values. The best fit was obtained by using the values of V_R as .7805 and 0.715. For these data points we obtain the following values of c_1 and $f_5(T_c)$:

$$c_1 = 0.0000035 \tag{F-14}$$

and

$$\ln f_5(T_c) = 9.706 \tag{F-15}$$

The fifth term evaluates ΔP_R as shown by the line A'BB'in Fig. F-3.

Proceeding similarly we obtain the following values for the sixth term:

$$a_2 = 22.00 \tag{F-16}$$

$$c_2 = 0.0000014 \tag{F-17}$$

$$\ln f_6(T_c) = 11.2377 \tag{F-18}$$

Equation (F-1) can be written in the reduced form for the critical isotherm as follows:

$$P_R = \frac{T_R}{Z_c(V_R - b/V_c} - \frac{3}{8Z_c^2(V_R - b/V_c)^2} + \frac{1}{16Z_c^3(V_R - b/V_c^3)}$$

$$- \frac{1}{256Z_c^4(V_R - b/V_c)^4} + \frac{e^{9.706}}{e^{16V_R}(1+3.5\text{x}10^{-6}e^{16V_R}}$$

$$+ \frac{e^{11.2377}}{e^{22V_R}(1+1.4\text{x}10^{-6}e^{22V_R}} \tag{F-19}$$

Equation (F-19) fits the critical isotherm data as shown in Table F-1. Equation (F-1) can be written in the reduced form as follows:

$$P_R = \frac{T_R}{Z_c\ (V_R-b/V_c)} + \frac{A_2'+B_2'T_R+C_2'e^{-kT_R}}{Z_c^{\ 2}(V_R-b/V_c)^2} + \frac{A_3'+B_3'T_R+C_3'e^{-kT_R}}{Z_c^{\ 3}(V_R-b/V_c)^3}$$

$$+ \frac{A_4'+B_4'T_R+C_4'e^{-kT_R}}{Z_c^{\ 4}(V_R-b/V_c)^4} + \frac{A_5'+B_5'T_R}{e^{a_1V_R}(1+c_1e^{a_1V_R})} + \frac{A_6'+B_6'T_R}{e^{a_2V_R}(1+c_2e^{a_2V_R})} \qquad \text{(F-20)}$$

where $f_i'(T_R = A_i' + B_i'\ T_R + C_i'\ e^{-kT_R})$

and the following relations can be easily proven.

$$f_2'(T_c) = -3/8 \qquad \text{(F-21)}$$

$$f_3'(T_c) = 1/16 \qquad \text{(F-22)}$$

$$f_4'(T_c) = -1/256 \qquad \text{(F-23)}$$

$$f_5'(T_c) = e^{-9.706} \qquad \text{(F-24)}$$

$$f_6'(T_c) = e^{11.2377} \qquad \text{(F-25)}$$

Till now, we have determined the following ten terms in the reduced equation of state (F-20)

$f_2'(T_c)$, $f_3'(T_c)$, $f_4'(T_c)$, $f_5'(T_c)$, $f_6'(T_c)$, a_1, c_1, a_2, c_2

and b

TABLE F-1

Critical Isotherm of R-22

********** COMPARISON OF EXPERIMENTAL CRITICAL ISOTHERM OF CHLORODIFLUROMETHANE WITH THE EQUATION OF STATE *****

V	PEXP	PCAL	PREXP	PRCAL	PCD	VR	RHOR	
0.621134	124.55	-0.00	0.1725	0.1725	0.04	20.3484	0.0491	2
0.483159	157.12	-0.00	0.2176	0.2176	0.01	15.8283	0.0632	2
0.395709	188.32	-0.00	0.2609	0.2608	0.01	12.9634	0.0771	2
0.332786	219.62	-0.00	0.3042	0.3042	0.02	10.9021	0.0917	2
0.279699	255.22	-0.00	0.3535	0.3535	-0.00	9.1629	0.1091	2
0.241840	288.44	-0.00	0.3996	0.3996	0.00	7.9227	0.1262	2
0.214540	318.08	-0.00	0.4406	0.4407	-0.01	7.0283	0.1423	2
0.206329	328.20	-0.00	0.4546	0.4547	-0.01	6.7593	0.1479	2
0.194169	343.50	-0.00	0.4758	0.4771	-0.26	6.3610	0.1572	1
0.171650	378.61	-0.00	0.5245	0.5246	-0.03	5.6233	0.1778	2
0.150000	418.50	-0.00	0.5797	0.5794	0.05	4.9140	0.2035	1
0.142540	433.52	-0.00	0.6005	0.6008	-0.04	4.6696	0.2142	2
0.122020	481.52	-0.00	0.6670	0.6674	-0.06	3.9974	0.2502	2
0.120470	485.38	-0.00	0.6724	0.6729	-0.08	3.9466	0.2534	2
0.105900	525.74	-0.00	0.7283	0.7288	-0.08	3.4693	0.2682	2
0.102030	538.00	-0.00	0.7452	0.7449	0.05	3.3425	0.2992	1
0.099210	545.89	-0.00	0.7562	0.7569	-0.09	3.2501	0.3077	2
0.093570	563.79	-0.00	0.7810	0.7816	-0.08	3.0654	0.3262	2
0.084310	593.00	-0.00	0.8214	0.8243	-0.35	2.7620	0.3621	1
0.083890	595.94	-0.00	0.8255	0.8263	-0.09	2.7482	0.3639	2
0.081554	603.98	-0.00	0.8366	0.8374	-0.09	2.6717	0.3743	2
0.075770	624.05	-0.00	0.8644	0.8653	-0.09	2.4822	0.4029	2
0.074500	625.50	-0.00	0.8665	0.8714	-0.57	2.4406	0.4097	1
0.066950	654.74	-0.00	0.9070	0.9077	-0.08	2.1933	0.4559	2
0.064591	658.00	-0.00	0.9115	0.9187	-0.79	2.1160	0.4726	1

0.057620	685.00	-0.00	0.9489	0.9495	-0.06	1.8876	0.5298	1
0.054760	693.29	-0.00	0.9604	0.9608	-0.05	1.7939	0.5574	2
0.051672	700.00	-0.00	0.9697	0.9719	-0.23	1.6928	0.5907	1
0.046296	712.00	-0.00	0.9863	0.9873	-0.10	1.5167	0.6593	1
0.044478	715.47	-0.00	0.9911	0.9912	-0.01	1.4571	0.6863	2
0.042488	718.00	-0.00	0.9946	0.9946	-0.00	1.3919	0.7184	1
0.037339	721.40	-0.00	0.9993	0.9993	-0.00	1.2232	0.8175	1
0.035992	721.60	-0.00	0.9996	0.9997	-0.02	1.1791	0.8481	2
0.030525	721.90	-0.00	1.0000	1.0001	-0.01	1.0000	1.0000	2
0.029308	722.20	-0.00	1.0004	1.0001	0.03	0.9601	1.0415	2
0.028528	721.91	-0.00	1.0000	1.0001	-0.01	0.9346	1.0700	4
0.028264	721.92	-0.00	1.0000	1.0001	-0.01	0.9259	1.0800	4
0.028005	721.94	-0.00	1.0000	1.0001	-0.01	0.9174	1.0900	4
0.027750	721.96	-0.00	1.0001	1.0001	-0.01	0.9091	1.1000	4
0.027254	722.04	-0.00	1.0002	1.0002	0.00	0.8928	1.1200	4
0.026776	722.20	-0.00	1.0004	1.0002	0.02	0.8772	1.1400	4
0.026315	722.44	-0.00	1.0007	1.0004	0.03	0.8621	1.1600	4
0.025869	722.82	-0.00	1.0013	1.0007	0.06	0.8475	1.1800	4
0.025438	723.39	-0.00	1.0021	1.0013	0.08	0.8333	1.2000	4
0.025021	724.19	-0.00	1.0032	1.0022	0.10	0.8197	1.2200	4
0.024617	725.29	-0.00	1.0047	1.0036	0.11	0.8065	1.2400	4
0.024226	726.88	-0.00	1.0069	1.0056	0.13	0.7936	1.2600	4
0.023848	728.76	-0.00	1.0095	1.0083	0.12	0.7813	1.2800	4
0.023824	727.91	-0.00	1.0083	1.0085	-0.02	0.7805	1.2813	2
0.023481	731.43	-0.00	1.0132	1.0119	0.12	0.7692	1.3000	4
0.023181	734.00	-0.00	1.0168	1.0158	0.10	0.7594	1.3168	1
0.023125	734.53	-0.00	1.0175	1.0166	0.09	0.7576	1.3200	4
0.022780	736.50	-0.00	1.0230	1.0224	0.06	0.7463	1.3400	4
0.022445	743.56	-0.00	1.0300	1.0295	0.04	0.7353	1.3600	4
0.022120	749.33	-0.00	1.0380	1.0381	-0.01	0.7247	1.3800	4

0.021824	755.00	-0.00	1.0458	1.0477	-0.17	0.7150	1.3987	1
0.021804	756.55	-0.00	1.0480	1.0484	-0.04	0.7143	1.4000	4
0.021052	780.37	-0.00	1.0810	1.0824	-0.13	0.6897	1.4500	4
0.020350	814.30	-0.00	1.1280	1.1312	-0.29	0.6667	1.5000	4
0.019630	868.00	-0.00	1.2024	1.2078	-0.45	0.6431	1.5550	1
0.019078	927.64	-0.00	1.2850	1.2936	-0.67	0.6250	1.6000	4
0.018454	1024.00	-0.00	1.4165	1.4321	-0.96	0.6046	1.6541	1
0.017778	1186.00	-0.00	1.6429	1.6540	-0.67	0.5824	1.7170	1
0.017169	1365.00	-0.00	1.8908	1.9454	-2.89	0.5625	1.7779	1
0.016721	1612.00	-0.00	2.2330	2.2358	-0.12	0.5478	1.8255	1
0.016213	1915.00	-0.00	2.6527	2.6678	-0.57	0.5311	1.8827	1
0.015766	2282.00	-0.00	3.1611	3.1639	-0.09	0.5165	1.9361	1
0.015299	2768.00	-0.00	3.8343	3.8301	0.11	0.5012	1.9952	3
0.015263	2794.00	-0.00	3.8703	3.8888	-0.48	0.5000	1.9999	3
0.014536	3855.00	-0.00	5.3400	5.3518	-0.22	0.4762	2.1000	3
0.013875	5349.00	-0.00	7.4095	7.2584	2.04	0.4545	2.2000	3
0.013272	7327.00	-0.00	10.1495	9.6347	5.07	0.4348	2.3000	3
0.012719	9890.00	-0.00	13.6998	12.4752	8.94	0.4167	2.4000	3
0.012210	13174.99	-0.00	18.2503	15.7201	13.86	0.4000	2.5000	3
0.011740	17397.99	-0.00	24.1001	19.2389	20.17	0.3846	2.6001	3
0.011306	22955.99	-0.00	31.7991	22.8009	28.30	0.3704	2.6999	3
0.010902	29886.99	-0.00	41.4001	26.0942	36.97	0.3571	2.7999	3
0.010526	39126.98	-0.00	54.1996	28.6416	47.16	0.3448	2.9000	3

---

1 = Zander (140)
2 = Michels (99)
3 = Values obtained from Fig. F-1
4 = Values obtained from Fig. F-2

We need nine more conditions to evaluate all the constants in Equation (F-20). From the complete description of generalized behavior of gases as analyzed by Martin (89), the nine conditions for R-22 are as follows:

1) Set $k = 3.0$ (from analysis of PVT data of R-22)

2) Set $\frac{BP_c}{RT} = -0.740$ at $T = 0.8T_c$

3) $\frac{BP_c}{RT} = 0.0$ at $T = T_B = 2.3T_c$

4) $\left(\frac{dP_R}{dT_R}\right)_{1.5V_c, T \to \infty} = 3.95$

5) $\left(\frac{dP_R}{dT_R}\right)_{\rho_c} = 7.40 = M$

6) $\left(\frac{dP_R}{dT_R}\right)_{1.4\rho_c, T\to\infty} = 14.10 = 1.9M$

7) $\left(\frac{dP_R}{dT_R}\right)_{1.8\rho_c} = 23.80 = 3.2M$

8) $\left(\frac{d^2P_R}{dT_R^2}\right)_{\rho_c} = 0.0$

9) $\left(\frac{d^2P_R}{dT_R^2}\right)_{1.8\rho_c} = 0.0$

Equations for derivatives are as follows:

$$\frac{dP_R}{dT_R} = \frac{1}{Z_c(V_R-b/V_c)} + \frac{B_2'-C_2'\,ke^{-kT_R}}{Z_c^{\,2}(V_R-b/V_c)^2} + \frac{B_3'-C_3'\,ke^{-kT_R}}{Z_c^{\,3}(V_R-b/V_c)^3}$$

$$+ \frac{B_4'-C_4'\,ke^{-kT_R}}{Z_c^{\,4}(V_R-b/V_c)^4} + \frac{B_5'}{e^{a_1V_R}(1+c_1e^{a_1V_R})} + \frac{B_6'}{e^{a_2V_R}(1+c_2e^{a_2V_R})} \qquad \text{(F-26)}$$

$$\frac{d^2P_R}{dT_R^{\,2}} = \frac{C_2'k^2e^{-kT_R}}{Z_c^{\,2}(V_R-b/V_c)^2} + \frac{C_3'k^2e^{-kT_R}}{Z_c^{\,3}(V_R-b/V_c)^3} + \frac{C_4'k^2e^{-kT_R}}{Z_c^{\,4}(V_R-b/V_c)^4} \qquad \text{(F-27)}$$

Using the conditions (2) and (3) with the value of $f_2'(T_c)$, A_2', B_2', and C_2' were calculated for R-22. To evaluate the rest of the constants ten simultaneous equations were solved on the computer. Equations (F-20), (F-26), and (F-27) are easy for hand calculations also. Listing of the computer program is given at the end of this section. The experimental PVT data of R-22 is compared with this equation in Tables V-1, V-2, and V-3.

The experimental PVT data of R-22 was analyzed to obtain the isochore slopes at the critical temperature. This information is presented in Table F-3 and Fig. F-4.

TABLE F-3. ISOCHORE SLOPES FOR R-22

No:	Density lbs/cu.ft.	Isochore Slope (dp/dT)V psi/F	Reference
1	1.61	0.2139	99
2	2.070	0.2817	99
3	2.527	0.3488	99
4	3.005	0.4255	99
5	3.575	0.5155	99
6	4.135	0.6030	99
7	4.661	0.6944	99
8	4.847	0.7362	99
9	5.150	0.7742	140
10	5.826	0.9091	99
11	6.667	1.093	140
12	7.016	1.130	99
13	8.195	1.37-	99
14	9.443	1.640	99
15	9.801	1.702	140
16	10.080	1.772	99
17	10.687	1.887	99
18	11.861	2.198	140
19	11.920	2.264	99
20	12.262	2.381	99
21	13.198	2.540	99
22	13.422	2.553	140
23	14.937	2.892	99
24	15.482	3.030	140
25	17.355	3.577	140
26	18.262	3.721	99
27	19.353	4.156	140
28	21.600	4.731	140
29	22.483	4.835	99
30	23.536	5.217	140
31	26.782	5.714	140

TABLE F-3 (contd.)

No.	Density lbs/cu.ft.	Isochore Slopes (dp/dT)V psi/F	Reference
32	27.784	6.429	99
33	29.778	7.037	140
34	33.274	8.205	140
35	34.120	8.571	99
36	38.955	10.91	140
37	41.975	12.08	99
38	43.138	12.50	140
39	45.138	13.79	140
40	50.942	16.67	140
41	54.188	20.00	140
42	56.188	22.22	140
43	58.246	24.00	140
44	59.806	27.00	140
45	61.679	28.88	140
46	63.427	31.75	140
47	65.363	33.33	140
48	66.986	38.52	140
49	68.359	39.68	140
50	69.670	40.78	140
51	70.919	44.64	140
52	72.230	48.08	140
53	73.790	52.63	140
54	75.039	58.14	140
55	76.038	60.24	140
56	77.099	60.98	140
57	77.973	62.5	140

ρ_c = 32.76 lbs/cu.ft.

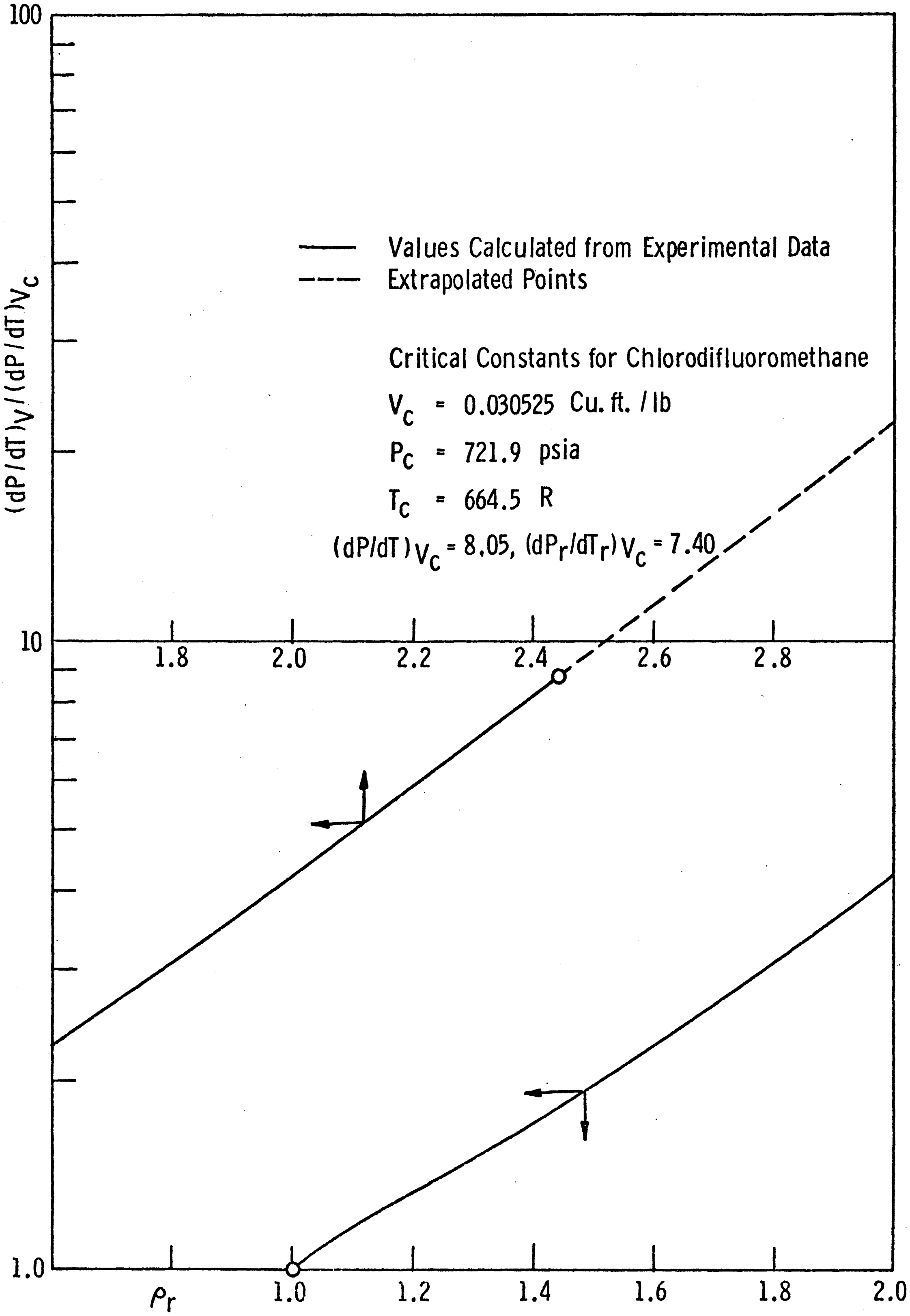

Fig. F. 4. Plot of $[(dP/dT)_V/(dP/dT)_{V_c}]$ vs ρ_r For R-22 at the Critical Temperature

Computer Program to Correlate PVT Behavior of R-22 with Eqn. (F-20)

```
MICHIGAN TERMINAL SYSTEM FORTRAN G(41336)              MAIN              01-05-73          20:10.23          PAGE P001

  0001                 IMPLICIT REAL*8(A-H,O-Z,$)                                                          5.000
  0002                 DIMENSION PROR(15),TTR(15),BT(3),SLP1(10),SLP2(15),FTC(10),                         6.000
                      1AAA(3,3),BB(3),AA(10,10),BBB(10),VVR(15),FF(10),PCDEV(200),                         7.000
                      2STC(3),SLP2C(10),SLP1C(10)                                                          8.000
  0003                 COMMON A(10),B(10),C(10),AE5,CC5,AE6,CC6,EX,BAA,R,ZC,AK                             9.000
  0004                 NAMELIST /DATA1/ TC,VC,PC                                                          10.000
  0005                 NAMELIST /DATA2/ AK,R,ZCV                                                          11.000
  0006                 NAMELIST /DATA3/ CC5,AE5,ALGF5                                                     12.000
  0007                 NAMELIST /DATA4/ CC6,AE6,ALGF6                                                     13.000
  0008                 NAMELIST /DATA5/ RO5,SL15                                                          14.000
  0009                 NAMELIST /DATA6/ RO6,SL16                                                          15.000
  0010                 NAMELIST /DATA7/ TT7,RO7,SL17                                                      16.000
  0011                 NAMELIST /DATA8/ TT8,RO8,SL18                                                      17.000
  0012                 NAMELIST /DATA9/ TT9,RO9,SL29                                                      18.000
  0013                 NAMELIST /DATA10/ TT10,RO10,SL210                                                  19.000
  0014                 NAMELIST /DATA11/ TT1,BT1,TT2,BT2                                                  20.000
                 C   ***** READ THE DATA                                                                  21.000
  0015                 READ (5,DATA1)                                                                     22.000
  0016                 READ (5,DATA2)                                                                     23.000
  0017                 READ (5,DATA3)                                                                     24.000
  0018                 READ (5,DATA4)                                                                     25.000
  0019                 READ (5,DATA5)                                                                     26.000
  0020                 READ (5,DATA6)                                                                     27.000
  0021                 READ (5,DATA7)                                                                     28.000
  0022                 READ (5,DATA8)                                                                     29.000
  0023                 READ (5,DATA9)                                                                     30.000
  0024                 READ (5,DATA10)                                                                    31.000
  0025                 READ (5,DATA11)                                                                    32.000
                 C   ***** DIMENSIONALIZING  THE  INPUT  VARIABLES                                        33.000
  0026                 PROR(5)=RO5                                                                        34.000
  0027                 PROR(6)=RO6                                                                        35.000
  0028                 PROR(7)=RO7                                                                        36.000
  0029                 PROR(8)=RO8                                                                        37.000
  0030                 PROR(9)=RO9                                                                        38.000
  0031                 PROR(10)=RO10                                                                      39.000
  0032                 TTR(1)=TT1                                                                         40.000
  0033                 TTR(2)=TT2                                                                         41.000
  0034                 TTR(7)=TT7                                                                         42.000
  0035                 TTR(8)=TT8                                                                         43.000
  0036                 TTR(9)=TT9                                                                         44.000
  0037                 TTR(10)=TT10                                                                       45.000
  0038                 BT(1)=BT1                                                                          46.000
  0039                 BT(2)=BT2                                                                          47.000
  0040                 SLP1(5)=SL15                                                                       48.000
  0041                 SLP1(6)=SL16                                                                       49.000
  0042                 SLP1(7)=SL17                                                                       50.000
  0043                 SLP1(8)=SL18                                                                       51.000
  0044                 SLP1(9)=SL113                                                                      52.000
  0045                 SLP2(9)=SL29                                                                       53.000
  0046                 SLP2(10)=SL210                                                                     54.000
                 C   ***** PRINT THE DATA                                                                 55.000
  0047                 WRITE (6,100)                                                                      56.000
  0048                 WRITE (6,101)                                                                      57.000
  0049            100  FORMAT ('1',//)                                                                    58.000
  0050            101  FORMAT ('0','*******  INPUT  DATA  TO  SOLVE  COEFFICIENTS  IN                     59.000
```

```
MICHIGAN TERMINAL SYSTEM FORTRAN G(41336)          MAIN            01-05-73         20:10.23          PAGE P002

                1THE  REDUCED  EQUATION  OF  STATE  **')                                          60.000
 0051             WRITE (6,110) TC,VC,PC                                                          61.000
 0052             WRITE (6,111) AK,R,ZCV                                                          62.000
 0053             WRITE (6,112) CC5,AE5,ALGF5                                                     63.000
 0054             WRITE (6,113) CC6,AE6,ALGF6                                                     64.000
 0055             WRITE (6,114) TTR(1),BT(1),TTR(2),BT(2)                                         65.000
 0056             WRITE (6,115) RROR(5),SLP1(5)                                                   66.000
 0057             WRITE (6,115) RROR(6),SLP1(6)                                                   67.000
 0058             WRITE (6,117) TTR(7),RROR(7),SLP1(7)                                            68.000
 0059             WRITE (6,117) TTR(8),RROR(8),SLP1(8)                                            69.000
 0060             WRITE (6,120) TTR(9),RROR(9),SLP2(9)                                            70.000
 0061             WRITE (6,120) TTR(10),RROR(10),SLP2(10)                                         71.000
 0062         110 FORMAT ('0',10X,'TC = ',F10.2,10X,'VC = ',F10.6,10X,'PC = ',F10.3)              72.000
 0063         111 FORMAT ('0',10X,'AK = ',F10.2,10X,'R  = ',F10.6,10X,'ZCV= ',F10.4)              73.000
 0064         112 FORMAT ('0',10X,'CC5= ',F10.2,10X,'AE5= ',F10.6,10X,'ALGF5= ',F10.              74.000
                1 6)                                                                              75.000
 0065         113 FORMAT ('0',10X,'CC6= ',F10.2,10X,'AE6= ',F10.6,10X,'ALGF6= ',F10.              76.000
                1 6)                                                                              77.000
 0066         114 FORMAT ('0',10X,'TTR= ',F10.2,5X, 'BT = ',F10.4,10X,'TTR= ',F10.2,              78.000
                15X,'BT = ',F10.4)                                                                79.000
 0067         115 FORMAT ('0',35X,'ROR= ',F10.6,10X,'SLP1 = ',F6.2)                               80.000
 0068         117 FORMAT ('0',10X,'TTR= ',F10.2,10X,'ROR= ',F10.6,10X,'SLP1 = ',F6.2              81.000
                1)                                                                                82.000
 0069         120 FORMAT ('0',10X,'TTR= ',F10.2,10X,'RCR= ',F10.6,10X,'SLP2 = ',F6.2              83.000
                1)                                                                                84.000
            C   *****  ADDITIONAL  FACTS  OF  CRITICAL  ISOTHERM  AND  OTHER                      85.000
            C RELATIONS                                                                           85.000
 0070             EX=170.000                                                                      86.000
 0071             ZC=PC*VC/(R*TC)                                                                 87.000
 0072             FTC(2)=-3./8.                                                                   88.000
 0073             FTC(3)=1./16.                                                                   89.000
 0074             FTC(4)=-1./256.                                                                 90.000
 0075             FTC(5)=DEXP(ALGF5)                                                              91.000
 0076             FTC(6)=DEXP(ALGF6)                                                              92.000
 0077             FTC(7)=DEXP(ALGF7)                                                              93.000
 0078             BT(3)=-0.375+(ZCV-0.25)                                                         94.000
 0079             TTR(3)=1.0                                                                      95.000
 0080             BA=ZCV-0.250                                                                    96.000
 0081             BAA=BA/ZC                                                                       97.000
 0082             ZC2=ZC*ZC                                                                       98.000
 0083             ZC3=ZC*ZC2                                                                      99.000
 0084             ZC4=ZC*ZC3                                                                     100.000
            C  ***** CALCULATION  OF  A2,B2,C2                                                   101.000
            C  ***** MATRIX  ELEMENTS  ARE                                                       102.000
 0085             DO 201 J=1,3                                                                   103.000
 0086             AKTR=-AK*TTR(J)                                                                104.000
 0087             AAA(J,1)=1.0                                                                   105.000
 0088             AAA(J,2)=TTR(J)                                                                106.000
 0089             AAA(J,3)=DEXP(AKTR)                                                            107.000
 0090        201  BB(J)=TTR(J)*TTR(J)*(BT(J)-BA/TTR(J))                                          108.000
 0091             CALL DGELG (BB,AAA,3,1,1.E-15,IER)                                             109.000
 0092             A(2)=BB(1)                                                                     110.000
 0093             B(2)=BB(2)                                                                     111.000
 0094             C(2)=BB(3)                                                                     112.000
            C  *****  CALCULATION  OF  A3,B3,....B6 (TEN  CONSTANTS)                             113.000
```

```
                 C   *****   CONDITIONS  ARE                                               114.000
                 C   *****   F3TC,F4TC,F5TC,F6TC                    ( 4  CONDITIONS)       115.000
                 C   *****   DP/DT  AT  RHOR5,RHOR6  AS  T  INFINITY( 2  CONDITIONS)       116.000
                 C   *****   DP/DT  AT  RHOR7,RHOR8  AT  T=TC       ( 2  CONDITIONS)       117.000
                 C   *****   D2P/DT2  AT  RHOR9,RHOR10  AT  T=TC    ( 2  CONDITIONS)       118.000
                 C   *****   TEN  TOTAL  CONDITIONS                                        119.000
                 C   *****   MATRIX  ELEMENTS  ARE:                                        120.000
   0095                 XX=DEXP(-AK)                                                       121.000
   0096                 AA(1,1)=1.0                                                        122.000
   0097                 AA(1,2)=0.0                                                        123.000
   0098                 AA(1,3)=0.0                                                        124.000
   0099                 AA(1,4)=0.0                                                        125.000
   0100                 AA(1,5)=1.0                                                        126.000
   0101                 AA(1,6)=0.0                                                        127.000
   0102                 AA(1,7)=0.0                                                        128.000
   0103                 AA(1,8)=0.0                                                        129.000
   0104                 AA(1,9)=XX                                                         130.000
   0105                 AA(1,10)=0.0                                                       131.000
   0106                 BBB(1)=FTC(3)                                                      132.000
   0107                 AA(2,1)=0.0                                                        133.000
   0108                 AA(2,2)=1.0                                                        134.000
   0109                 AA(2,3)=0.0                                                        135.000
   0110                 AA(2,4)=0.0                                                        136.000
   0111                 AA(2,4)=0.0                                                        137.000
   0112                 AA(2,5)=0.0                                                        138.000
   0113                 AA(2,6)=1.0                                                        139.000
   0114                 AA(2,7)=0.0                                                        140.000
   0115                 AA(2,8)=0.0                                                        141.000
   0116                 AA(2,9)=0.0                                                        142.000
   0117                 AA(2,10)=XX                                                        143.000
   0118                 BBB(2)=FTC(4)                                                      144.000
   0119                 AA(3,1)=0.0                                                        145.000
   0120                 AA(3,2)=0.0                                                        146.000
   0121                 AA(3,3)=1.0                                                        147.000
   0122                 AA(3,4)=0.0                                                        148.000
   0123                 AA(3,5)=0.0                                                        149.000
   0124                 AA(3,6)=0.0                                                        150.000
   0125                 AA(3,7)=1.0                                                        151.000
   0126                 AA(3,8)=0.0                                                        152.000
   0127                 AA(3,9)=0.0                                                        153.000
   0128                 AA(3,10)=0.0                                                       154.000
   0129                 BBB(3)=FTC(5)                                                      155.000
   0130                 AA(4,1)=0.0                                                        156.000
   0131                 AA(4,2)=0.0                                                        157.000
   0132                 AA(4,3)=0.0                                                        158.000
   0133                 AA(4,4)=1.0                                                        159.000
   0134                 AA(4,5)=0.0                                                        160.000
   0135                 AA(4,6)=0.0                                                        161.000
   0136                 AA(4,7)=0.0                                                        162.000
   0137                 AA(4,8)=1.0                                                        163.000
   0138                 AA(4,9)=0.0                                                        164.000
   0139                 AA(4,10)=0.0                                                       165.000
   0140                 BBB(4)=FTC(6)                                                      166.000
   0141                 DO 202 I=5,10                                                      167.000
   0142          202    VVR(I)=1./RROR(I)                                                  168.000
```

```
 0143          DO 207 I=5,6                                            169.000
 0144          AA(I,1)=0.0                                             170.000
 0145          AA(I,2)=0.0                                             171.000
 0146          AA(I,3)=0.0                                             172.000
 0147          AA(I,4)=0.0                                             173.000
 0148          VRB1=VVR(I)-BAA                                         174.000
 0149          VRB2=VRB1*VRB1                                          175.000
 0150          VRB3=VRB2*VRB1                                          176.000
 0151          VRB4=VRB3*VRB1                                          177.000
 0152          AA(I,5)=(1./ZC3)/(VRB3)                                 178.000
 0153          AA(I,6)=(1./ZC4)/VRB4                                   179.000
 0154          EXP5=AE5*VVR(I)                                         180.000
 0155          EXP6=AE6*VVR(I)                                         181.000
 0156          IF (EXP5.GT.EX) GO TO 203                               182.000
 0157          AA(I,7)=(1./DEXP(EXP5))/(1.+CC5*DEXP(EXP5))             183.000
 0158          AA(I,7)=(1./DEXP(EXP5))/(1.+CC5*DEXP(EXP5))             184.000
 0159          GO TO 204                                               185.000
 0160     203  AA(I,7)=0.0                                             186.000
 0161     204  IF (EXP6.GT.EX) GO TO 205                               187.000
 0162          AA(I,8)=(1./DEXP(EXP6))/(1.+CC6*DEXP(EXP6))             188.000
 0163          GO TO 206                                               189.000
 0164     205  AA(I,8)=0.0                                             190.000
 0165     206  CONTINUE                                                191.000
 0166     207  BBB(I)=SLP1(I)-1./(ZC*VRB1) - B(2)/(ZC2*VRB2)           192.000
 0167          DO 212 I=7,8                                            193.000
 0168          VRB1=VVR(I)-BAA                                         194.000
 0169          VRB2=VRB1*VRB1                                          195.000
 0170          VRB3=VRB1*VRB2                                          196.000
 0171          VRB4=VRB1*VRB3                                          197.000
 0172          EXP5=AE5*VVR(I)                                         198.000
 0173          EXP6=AE6*VVR(I)                                         199.000
 0174          AKTR=-AK*TTR(I)                                         200.000
 0175          XX= AK*DEXP(AKTR)                                       201.000
 0176          AA(I,1)=0.0                                             202.000
 0177          AA(I,2)=0.0                                             203.000
 0178          AA(I,3)=0.0                                             204.000
 0179          AA(I,4)=0.0                                             205.000
 0180          AA(I,5)=1./(ZC3*VRB3)                                   206.000
 0181          AA(I,6)=1./(ZC4*VRB4)                                   207.000
 0182          IF (EXP5.GT.EX) GO TO 208                               208.000
 0183          AA(I,7)=(1./DEXP(EXP5))/(1.+CC5*DEXP(EXP5))             209.000
 0184          GO TO 209                                               210.000
 0185     208  AA(I,7)=0.0                                             211.000
 0186     209  IF (EXP6.GT.EX) GO TO 210                               212.000
 0187          AA(I,8)=(1./DEXP(EXP6))/(1.+CC6*DEXP(EXP6))             213.000
 0188          GO TO 211                                               214.000
 0189     210  AA(I,8)=0.0                                             215.000
 0190     211  AA(I,9)=-XX/(ZC3*VRB3)                                  216.000
 0191          AA(I,10)=-XX/(ZC4*VRB4)                                 217.000
 0192     212  BBB(I)=SLP1(I)-1./(ZC*VRB1) -(B(2)-XX*C(2))/(ZC2*VRB2)  218.000
 0193          DO 214 I=9,10                                           219.000
 0194          AKTR=-AK*TTR(I)                                         220.000
 0195          XX=AK*AK*DEXP(AKTR)                                     221.000
 0196          VRB1=VVR(I)-BAA                                         222.000
 0197          VRB2=VRB1*VRB1                                          223.000
```

```
MICHIGAN TERMINAL SYSTEM FORTRAN G(41336)          MAIN          01-05-73          20:10.23          PAGE P005

 0198               VRB3=VRB1*VRB2                                                             224.000
 0199               VRB4=VRB1*VRB3                                                            ,225.000
 0200               DO 213 J=1,8                                                               226.000
 0201          213  AA(I,J)=0.0                                                                227.000
 0202               AA(I,9)=XX/(ZC3*VRB3)                                                      228.000
 0203               AA(I,10)=XX/(ZC4*VRB4)                                                     229.000
 0204          214  BBB(I)=SLP2(I)-XX*C(2)/(ZC2*VRB2)                                          230.000
 0205               WRITE (6,100)                                                              231.000
 0206               DO 221 I=1,10                                                              232.000
 0207          221  WRITE (6,121) (AA(I,J),J=1,10),BBB(I)                                      233.000
 0208          121  FORMAT (11E10.4)                                                           234.000
             C  ***** ALL  COEFFICIENTS  IN  AA  &  BBB  ARE  DEFINED                          235.000
 0209               CALL CSELG (BBB,AA,10,1,1.E-40,IES)                                        236.000
 0210               A(3)=BBB(1)                                                                237.000
 0211               A(4)=BBB(2)                                                                238.000
 0212               A(5)=BBB(3)                                                                239.000
 0213               A(6)=BBB(4)                                                                240.000
 0214               B(3)=BBB(5)                                                                241.000
 0215               B(4)=BBB(6)                                                                242.000
 0216               B(5)=BBB(7)                                                                243.000
 0217               B(6)=BBB(8)                                                                244.000
 0218               C(3)=BBB(9)                                                                245.000
 0219               C(4)=BBB(10)                                                               246.000
 0220               C(5)=0.0                                                                   247.000
 0221               C(6)=0.0                                                                   248.000
             C  ***** ALL  CONSTANTS  ARE  CALCULATED                                          249.000
             C  ***** PRINT  CONSTANTS                                                         250.000
 0222               WRITE (6,100)                                                              251.000
 0223               WRITE (6,122)                                                              252.000
 0224               WRITE (6,123)                                                              253.000
 0225               WRITE (6,124)                                                              254.000
 0226          122  FORMAT ('0','******  COEFFICIENTS  IN  THE  REDUCED  EQUATION  OF          255.000
                   1STATE  *******')                                                           256.000
 0227          123  FORMAT ('0',' ******  PR=TR/(ZC*(VR-B/VC))+(A2+B2*TR+C2*EXP(-K*TR)         257.000
                   1)/(ZC2*(VR-B/VC)*(VR-B/VC))+.....+(A5+B5*TR)/(EXP(AE5*VR))*(1.+CC5         258.000
                   2*EXP(AE5*VR)))+   ')                                                       259.000
 0228          124  FORMAT ('0','(A6+B6*TR)/(EXP(AE6*VR)*(1.+CC6*EXP(AE6*VR))) ***')           260.000
 0229               WRITE (6,102) IER                                                          261.000
 0230               WRITE (6,102) IES                                                          262.000
 0231               WRITE (6,131) A(2)                                                         263.000
 0232               WRITE (6,132) B(2)                                                         264.000
 0233               WRITE (6,133) C(2)                                                         265.000
 0234               WRITE (6,134) A(3)                                                         266.000
 0235               WRITE (6,135) B(3)                                                         267.000
 0236               WRITE (6,136) C(3)                                                         268.000
 0237               WRITE (6,137) A(4)                                                         269.000
 0238               WRITE (6,138) B(4)                                                         270.000
 0239               WRITE (6,139) C(4)                                                         271.000
 0240               WRITE (6,140) A(5)                                                         272.000
 0241               WRITE (6,141) B(5)                                                         273.000
 0242               WRITE (6,142) A(6)                                                         274.000
 0243               WRITE (6,143) B(6)                                                         275.000
 0244               WRITE (6,144) ZC                                                           276.000
 0245               WRITE (6,145) BAA                                                          277.000
 0246          102  FORMAT ('0',20X,'IE= ',I2)                                                 278.000
```

```
MICHIGAN TERMINAL SYSTEM FORTRAN G(41336)           MAIN          01-05-73         20:10.23          PAGE P006

 0247        131   FORMAT ('0',20X,'A(2)= ',E12.6)                                      279.000
 0248        132   FORMAT ('0',20X,'B(2)= ',E12.6)                                      280.000
 0249        133   FORMAT ('0',20X,'C(2)= ',E12.6)                                      281.000
 0250        134   FORMAT ('0',20X,'A(3)= ',E12.6)                                      282.000
 0251        135   FORMAT ('0',20X,'B(3)= ',E12.6)                                      283.000
 0252        136   FORMAT ('0',20X,'C(3)= ',E12.6)                                      284.000
 0253        137   FORMAT ('0',20X,'A(4)= ',E12.6)                                      285.000
 0254        138   FORMAT ('0',20X,'B(4)= ',E12.6)                                      286.000
 0255        139   FORMAT ('0',20X,'C(4)= ',E12.6)                                      287.000
 0256        140   FORMAT ('0',20X,'A(5)= ',E12.6)                                      288.000
 0257        141   FORMAT ('0',20X,'B(5)= ',E12.6)                                      289.000
 0258        142   FORMAT ('0',20X,'A(6)= ',E12.6)                                      290.000
 0259        143   FORMAT ('0',20X,'B(6)= ',E12.6)                                      291.000
 0260        144   FORMAT ('0',20X,'ZC  = ',F12.6)                                      292.000
 0261        145   FORMAT ('0',20X,'BAA = ',F12.6)                                      293.000
            C  ***** RECALCULATION  OF  INPUT  CONDITIONS                               294.000
 0262              WRITE (6,100)                                                        295.000
 0263              WRITE (6,125)                                                        296.000
 0264        125   FORMAT ('0',' *****  RECALCULATION  OF  INPUT  CONDITIONS ****')     297.000
            C  *****  F3TC,....F6TC                                                     298.000
 0265              DO 231 I=3,6                                                         299.000
 0266              XX=DEXP(-AK)                                                         300.000
 0267              FF(I)=A(I)+B(I)+C(I)*XX                                              301.000
 0268        231   WRITE (6,232) TC,FTC(I),FF(I)                                        302.000
 0269        232   FORMAT ('0',20X,'TEMP= ',F10.2,5X,'F(TC)= ',E10.4,5X,'FCAL= ',E10.   303.000
                  14)                                                                   304.000
            C  *****  DP/DT  AS  T  GOES  TO  INFINITY                                  305.000
 0270              DO 237 I=5,6                                                         306.000
 0271              VRB1=VVR(I)-BAA                                                      307.000
 0272              VRB2=VRB1*VRB1                                                       308.000
 0273              VRB3=VRB1*VRB2                                                       309.000
 0274              VRB4=VRB1*VRB3                                                       310.000
 0275              EXP5=AE5*VVR(I)                                                      311.000
 0276              EXP6=AE6*VVR(I)                                                      312.000
 0277              TERM1=1./(ZC*VRB1)                                                   313.000
 0278              TERM2=B(2)/(ZC2*VRB2)                                                314.000
 0279              TERM3=B(3)/(ZC3*VRB3)                                                315.000
 0280              TERM4=B(4)/(ZC4*VRB4)                                                316.000
 0281              IF (EXP5.GT.EX) GO TO 233                                            317.000
 0282              TERM5=(B(5)/DEXP(EXP5))/(1.+CC5*DEXP(EXP5))                          318.000
 0283              GO TO 234                                                            319.000
 0284        233   TERM5=0.0                                                            320.000
 0285        234   IF (EXP6.GT.EX) GO TO 235                                            321.000
 0286              TERM6=(B(6)/DEXP(EXP6))/(1.+CC6*DEXP(EXP6))                          322.000
 0287              GO TO 236                                                            323.000
 0288        235   TERM6=0.0                                                            324.000
 0289        236   CONTINUE                                                             325.000
 0290              SLP1C(I)=TERM1+TERM2+TERM3+TERM4+TERM5+TERM6                         326.000
 0291        237   WRITE (6,238) VVR(I),SLP1(I),SLP1C(I)                                327.000
 0292        238   FORMAT ('0',41X,'VOL= ',F10.6,5X,'SLOPE= ',F10.2,5X,'SLPCAL= ',F10   328.000
                  1.2)                                                                  329.000
            C  ***** DP/DT  AT  T=TC                                                    330.000
 0293              DO 239 I=7,8                                                         331.000
 0294              VR=VVR(I)                                                            332.000
 0295              TR=TTR(I)                                                            333.000
```

```
MICHIGAN TERMINAL SYSTEM FORTRAN G(41336)           MAIN           01-05-73        20:10.23         PAGE P007

  0296              CALL DPDT(VR,TR,SLOPE)                                                      334.000
  0297              SLP1C(I)=SLOPE                                                              335.000
  0298          239 WRITE (6,240) TTR(I),VVR(I),SLP1(I),SLP1C(I)                                336.000
  0299          240 FORMAT ('0',20X,'TEMP= ',F10.2,5X,'VOL= ',F10.6,5X,'SLOPE= ',F10.2          337.000
                   1,5X,'SLPCAL= ',F10.2)                                                       338.000
  0300              DO 222 I=1,3                                                                339.000
  0301              AKTR=-AK*TTR(I)                                                             340.000
  0302              XX=DEXP(AKTR)                                                               341.000
  0303              BTC(I)=(A(2)+B(2)*TTR(I)+C(2)*XX)/(TTR(I)*TTR(I))                           342.000
  0304              BTC(I)=BTC(I)+BA/TTR(I)                                                     343.000
  0305          222 WRITE (6,223) TTR(I),BT(I),BTC(I)                                           344.000
  0306          223 FORMAT ('0',20X,'TEMP= ',F10.2,5X,'B  = ',F10.4,5X,'BCAL= ',F10.4)          345.000
               C  *****  D2P/DT2  AT   T=TC                                                     346.000
  0307              DO 241 I=9,10                                                               347.000
  0308              VR=VVR(I)                                                                   348.000
  0309              TR=TTR(I)                                                                   349.000
  0310              CALL D2PDT2(VR,TR,SLOPE2)                                                   350.000
  0311              SLP2C(I)=SLOPE2                                                             351.000
  0312          241 WRITE (6,242) TTR(I),VVR(I),SLP2(I),SLP2C(I)                                352.000
  0313          242 FORMAT ('0',20X,'TEMP= ',F10.2,5X,'VOL= ',F10.6,5X,'SL2= ',F10.2,5          353.000
                   1X,'SL2CAL= ',F10.2)                                                         354.000
               C  *****  LINEARITY  TESTING                                                     355.000
  0314              WRITE (6,100)                                                               356.000
  0315              WRITE (6,243)                                                               357.000
  0316          243 FORMAT ('0','*****  LINEARITY   TESTING   **********')                      358.000
  0317              DO 244 I=5,6                                                                359.000
  0318              PR=1.0                                                                      360.000
  0319              VR=VVR(I)                                                                   361.000
  0320              TR1=20.0                                                                    362.000
  0321              TR=TR1                                                                      363.000
  0322              CALL PRESOR(VR,TR,PR,PRCAL,DEV,PCD)                                         364.000
  0323              PR=PRCAL                                                                    365.000
  0324              PR1=PR                                                                      366.000
  0325              DEV=0.0                                                                     367.000
  0326              PCD=0.0                                                                     368.000
  0327              WRITE (6,251) VR,TR,PR,PRCAL,DEV,PCD                                        369.000
  0328              TR=21.0                                                                     370.000
  0329              PR=PR1+SLP1(I)*(TR-TR1)                                                     371.000
  0330              CALL PRESOR(VR,TR,PR,PRCAL,DEV,PCD)                                         372.000
  0331              WRITE (6,251) VR,TR,PR,PRCAL,DEV,PCD                                        373.000
  0332              TR=22.0                                                                     374.000
  0333              PR=PR1+SLP1(I)*(TR-TR1)                                                     375.000
  0334              CALL PRESOR(VR,TR,PR,PRCAL,DEV,PCD)                                         376.000
  0335          244 WRITE (6,251) VR,TR,PR,PRCAL,DEV,PCD                                        377.000
  0336          251 FORMAT ('0',F15.6,4F15.3,F14.2)                                             378.000
  0337              DO 245  I=7,8                                                               379.000
  0338              VR=VVR(I)                                                                   380.000
  0339              TR1=1.0                                                                     381.000
  0340              TR=TR1                                                                      382.000
  0341              CALL PRESOR(VR,TR,PR,PRCAL,DEV,PCD)                                         383.000
  0342              PR=PRCAL                                                                    384.000
  0343              PR1=PR                                                                      385.000
  0344              DEV=0.0                                                                     386.000
  0345              PCD=0.0                                                                     387.000
  0346              WRITE (6,251) VR,TR,PR,PRCAL,DEV,PCD                                        388.000
```

```
0347            TR=1.1                                                               389.000
0348            PR=PRI+SLP1(I)*(TR-TR1)                                              390.000
0349            CALL PRESOR(VR,TR,PR,PRCAL,DEV,PCD)                                  391.000
0350            WRITE (6,251) VR,TR,PR,PRCAL,DEV,PCD                                 392.000
0351            TR=1.2                                                               393.000
0352            PR=PRI+SLP1(I)*(TR-TR1)                                              394.000
0353            CALL PRESOR(VR,TR,PR,PRCAL,DEV,PCD)                                  395.000
0354       245  WRITE (6,251) VR,TR,PR,PRCAL,DEV,PCD                                 396.000
0355            WRITE (6,100)                                                        397.000
          C     ******   COMPARISON  OF  EXPERIMENTAL  CRITICAL  ISOTHERM  OF        398.000
          C     ******   CHLORODIFLUOROMETHANE  WITH  CALCULATED  POINTS             399.000
          C     ******   CRITICAL  ISOTHERM  IS  CONSTRUCTED  FROM  MICHELS'  DATA   400.000
          C     ******   AND  ZANDER'S  DATA,  WITH  EXTRAPOLATION  TO  2.9  RHOR    401.000
          C     ******   FOLLOWING  CRITICAL  ISOTHERM  OF  CARBON  DIOXIDE          402.000
          C     ******   INPUT  DATA  UNITS  ARE:                                    403.000
          C     ******   VOLUME  IN  CUBIC  FEET  PER  POUND                         404.000
          C     ******   PRESSURE  IN  PSIA                                          405.000
0356            WRITE (6,551)                                                        406.000
0357       551  FORMAT ('0','**********      COMPARISON  OF  EXPERIMENTAL  CRITICAL  407.000
               1 ISOTHERM  OF  CHLORODIFLUROMETHANE  WITH  THE  EQUATION  OF  STA    408.000
               2TE *****',/)                                                         409.000
0358            WRITE (6,555)                                                        410.000
0359       555  FORMAT ('0','                 V            PEXP          PCAL     PR 411.000
               1EXP          PRCAL          PCD          VR          RHOR',//)       412.000
0360       550  READ (5,304) V,PEXP,I                                                413.000
0361            TEST=DABS(V-1000.)                                                   414.000
0362            IF (TEST.LT.0.1) GO TO 555                                           415.000
0363            VR=V/VC                                                              416.000
0364            PR=PEXP/PC                                                           417.000
0365            TR=1.0                                                               418.000
0366            PREXP=PR                                                             419.000
0367            CALL PRESOR (VR,TR,PR,PRCAL,DEV,PCD)                                 420.000
0368            RHOR=1./VR                                                           421.000
0369            WRITE (6,552) V,PEXP,PCAL,PREXP,PRCAL,PCD,VR,RHOR,I                  422.000
0370            GO TO 550                                                            423.000
0371       555  CONTINUE                                                             424.000
0372       304  FORMAT (2F15.6,I1)                                                   425.000
0373       552  FORMAT ('0', 9X,F12.6,2F12.2,2F12.4,F12.2,2F12.4,10X,I1)             426.000
0374            WRITE (6,100)                                                        427.000
0375            N=0.                                                                 428.000
          C   *****   CHLORODIFLUOROMETHANE,F-22                                     429.000
          C   *****   ISOMETRIC  PVT  DATA  REPORTED  BY  MICHELS                    430.000
          C   *****   INPUT  DATA  UNITS  ARE:                                       431.000
          C   *****   VOLUME  IN  CUBIC  FEET  PER  POUND                            432.000
          C   *****   TEMPERATURE  IN  RANKINE                                       433.000
          C   *****   PRESSURE  IN  PSIA                                             434.000
0376            WRITE (6,511)                                                        435.000
0377       511  FORMAT ('0',' *****     CHLORODIFLUOROMETHANE,  ISOMETRIC  PVT  DA   436.000
               1TA  REPORTED  BY  MICHELS *****')                                    437.000
0378            WRITE (6,512)                                                        438.000
0379       512  FORMAT ('0','*****     INPUT  DATA  UNITS  ARE:  V  IN  CFT/LB,  T   439.000
               1 IN  R,  P  IN  PSIA. *****')                                        440.000
0380            WRITE (6,521)                                                        441.000
0381       521  FORMAT ('0',' ***********     OUTPUT  IN  ORDER: VR,TR,PREXP,PRCAL   442.000
               1,DEV,PCD   ***********')                                             443.000
```

```
0382              WRITE (6,372)                                                       444.000
0383         11   READ (5,301) V,T,PEXP                                               445.000
0384              TEST=DABS(V-2000.)                                                  446.000
0385              IF (TEST.LT.0.1) GO TO 12                                           447.000
0386              N=N+1                                                               448.000
0387              VR=V/VC                                                             449.000
0388              TR=T/TC                                                             450.000
0389              PR=PEXP/PC                                                          451.000
0390              CALL PRESOR (VR,TR,PR,PRCAL,DEV,PCD)                                452.000
0391              WRITE (6,361) VR,TR,PR,PRCAL,PCD                                    453.000
0392              PCDEV(N)=PCD                                                        454.000
0393              GO TO 11                                                            455.000
0394         12   CONTINUE                                                            456.000
0395              CALL DEVIAN (PCDEV,N,AVPCD,ABPCD,STPCD)                             457.000
0396              WRITE (6,100)                                                       458.000
0397              WRITE (6,362) AVPCD,ABPCD,STPCD                                     459.000
0398        361   FORMAT ('0',F15.6,3F15.3,F14.2)                                     460.000
0399        362   FORMAT ('0',20X,'AVPCD= ',F10.2,10X,'ABPCD= ',F10.2,10X,'STPCD= ',  461.000
                 1F10.2)                                                              462.000
0400              WRITE (6,100)                                                       463.000
0401              N=0.0                                                               464.000
           C  *****  CHLORODIFLUORCMETHANE,F-22                                       465.000
           C  *****   ISOMETRIC  PVT  DATA  REPORTED  BY  ZANDER                      466.000
           C  *****   INPUT  DATA  UNITS  ARE:                                        467.000
           C  *****   DENSITY  IN  GRAMS  PER  CC.                                    468.000
           C  *****   TEMPERATURE  IN  CENTIGRADE                                     469.000
           C  *****   PRESSURE  IN  BAR                                               470.000
           C  *****   CONVERSION  FACTORS  ARE:                                       471.000
           C  *****   ONE  BAR = 14.50383 PSIA.                                       472.000
           C  *****   ONE  GRAM  PER  CC. = 62.428327  POUNDS  PER  CFT.              473.000
0402              WRITE (6,513)                                                       474.000
0403        513   FORMAT ('0',' *****     CHLORODIFLUROMETHANE,F-22,  ISOMETRIC  PVT  475.000
                 1  DATA  REPORTED  BY  ZANDER *****')                                476.000
0404              WRITE (6,514)                                                       477.000
0405        514   FORMAT ('0',' *****      INPUT  UNITS  ARE:  RHO  IN  GMS/CC,  T  I 478.000
                 1N  C,  P  IN  BAR *****')                                           479.000
0406              WRITE (6,522)                                                       480.000
0407        522   FORMAT ('0',' **********      OUTPUT  IN  ORDER : RHO, T, P, V, T,  481.000
                 1PEXP, PCAL, DEV, PCD      ***********')                             482.000
0408              WRITE (6,373)                                                       483.000
0409         21   READ (5,302) RHO,TEMP,PRES                                          484.000
0410              TEST=DABS(RHO-3000.)                                                485.000
0411              IF (TEST.LT.0.1) GO TO 22                                           486.000
0412              N=N+1                                                               487.000
0413              PEXP=PRES*14.50383                                                  488.000
0414              V=1./(RHO*62.428327)                                                489.000
0415              T=(TEMP+273.15)*1.8                                                 490.000
0416              PR=PEXP/PC                                                          491.000
0417              VR=V/VC                                                             492.000
0418              TR=T/TC                                                             493.000
0419              CALL PRESOR (VR,TR,PR,PRCAL,DEV,PCD)                                494.000
0420              WRITE (6,363) RHO,TEMP,PRES,VR,TR,PR,PRCAL,PCD                      495.000
0421              PCDEV(N)=PCD                                                        496.000
0422              GO TO 21                                                            497.000
0423        363   FORMAT ('0',F12.4,2F12.2,1F12.6,3F12.3,F11.2)                       498.000
```

```
 0424           22  CONTINUE                                                                      499.000
 0425               CALL DEVIAN (PCDEV,N,AVPCD,ABPCD,STPCD)                                       500.000
 0426               WRITE (6,100)                                                                 501.000
 0427               WRITE (6,362) AVPCD,ABPCD,STPCD                                               502.000
 0428               WRITE (6,100)                                                                 503.000
 0429               N=0.                                                                          504.000
              C  *****    CHLORODIFLUOROMETHANE,F-22                                              505.000
              C  *****    ISOTHERMAL  PVT  DATA  REPORTED  BY  ZANDER                             506.000
              C  *****    INPUT  DATA  UNITS  ARE:                                                507.000
              C  *****    TEMPERATURE  IN  CENTIGRADE                                             508.000
              C  *****    PRESSURE  IN  BAR                                                       509.000
              C  *****    CONVERSION  FACTORS  ARE:                                               510.000
              C  *****    ONE  BAR = 14.50383 PSIA.                                               511.000
 0430               WRITE (6,515)                                                                 512.000
 0431          515  FORMAT ('0','CHLORODIFLUROMETHANE,F-22,  ISOTHERMAL  DATA  REPORTE            513.000
                   1D  BY  ZANDER *****')                                                         514.000
 0432               WRITE (6,516)                                                                 515.000
 0433          516  FORMAT ('0',' *****      INPUT  UNITS  ARE  : T  IN  C,  P  IN  BAR           516.000
                   1 ******')                                                                     517.000
 0434               WRITE (6,523)                                                                 518.000
 0435          523  FORMAT ('0',' **********      OUTPUT  IN  ORDER : T, P, Z, V, T, PE           519.000
                   1XP, PCAL, DEV, PCD **********')                                               520.000
 0436               WRITE (6,374)                                                                 521.000
 0437           31  READ (5,303) TEMP,PRES,Z                                                      522.000
 0438               TEST=DABS(TEMP-4000.)                                                         523.000
 0439               IF (TEST.LT.0.1) GO TO 32                                                     524.000
 0440               N=N+1                                                                         525.000
 0441               PEXP=PRES*14.50383                                                            526.000
 0442               T=(TEMP+273.15)*1.8                                                           527.000
 0443               V=(Z*R*T)/PEXP                                                                528.000
 0444               PR=PEXP/PC                                                                    529.000
 0445               VR=V/VC                                                                       530.000
 0446               TR=T/TC                                                                       531.000
 0447               CALL PRESOR (VR,TR,PR,PRCAL,DEV,PCD)                                          532.000
 0448               WRITE (6,364) TEMP,PRES,Z,VR,TR,PR,PRCAL,PCD                                  533.000
 0449               PCDEV(N)=PCD                                                                  534.000
 0450               GO TO 31                                                                      535.000
 0451           32  CONTINUE                                                                      536.000
 0452               CALL DEVIAN (PCDEV,N,AVPCD,ABPCD,STPCD)                                       537.000
 0453               WRITE (6,100)                                                                 538.000
 0454               WRITE (6,362) AVPCD,ABPCD,STPCD                                               539.000
 0455               WRITE (6,100)                                                                 540.000
 0456          364  FORMAT ('0',2F12.2,2F12.6,3F12.3,F11.2)                                       541.000
 0457          301  FORMAT (F20.6,2F15.6)                                                         542.000
 0458          302  FORMAT (3F15.3)                                                               543.000
 0459          303  FORMAT (1F20.6,2F15.6)                                                        544.000
 0460          372  FORMAT ('0','          VR              TR              PR                 545.000
                   1   PRCAL              PCD',//)                                                546.000
 0461          373  FORMAT ('0','     RHO          TEMP          PRES          V                547.000
                   1T            PEXP          PCAL          PCD',//)                             548.000
 0462          374  FORMAT ('0','     TEMP          PRES          Z             V                549.000
                   1 T             PEXP          PCAL          PCD',//)                           550.000
 0463               END                                                                           551.000
*OPTIONS IN EFFECT*  ID,EBCDIC,SOURCE,NOLIST,NODECK,LOAD,NOMAP
*OPTIONS IN EFFECT*  NAME = MAIN    , LINECNT =      57
```

```
MICHIGAN TERMINAL SYSTEM FORTRAN G(41336)          PRESOR          01-05-73          20:10.44          PAGE P001
  0001              SUBROUTINE PRESOR (VR,TR,PR,PRCAL,DEV,PCD)                                552.000
  0002              IMPLICIT REAL*8(A-H,O-Z,$)                                                553.000
  0003              COMMON A(10),B(10),C(10),AE5,CC5,AE6,CC6,EX,BAA,R,ZC,AK                   554.000
  0004              DIMENSION XNN(10),YY(5),ZCC(5)                                            555.000
  0005              ZCC(2)=ZC*ZC                                                              556.000
  0006              ZCC(3)=ZCC(2)*ZC                                                          557.000
  0007              ZCC(4)=ZCC(3)*ZC                                                          558.000
  0008              AKTR=-AK*TR                                                               559.000
  0009              XX=DEXP(AKTR)                                                             560.000
  0010              DO 261 I=2,6                                                              561.000
  0011         261  XNN(I)=A(I)+B(I)*TR+C(I)*XX                                               562.000
  0012              YY(1)=VR-BAA                                                              563.000
  0013              YY(2)=YY(1)*YY(1)                                                         564.000
  0014              YY(3)=YY(2)*YY(1)                                                         565.000
  0015              YY(4)=YY(3)*YY(1)                                                         566.000
  0016              EXP5=AE5*VR                                                               567.000
  0017              EXP6=AE6*VR                                                               568.000
  0018              SUM=0.0                                                                   569.000
  0019              DO 262 I=2,4                                                              570.000
  0020              XNUM=(XNN(I)/YY(I))/ZCC(I)                                                571.000
  0021         262  SUM=SUM+XNUM                                                              572.000
  0022              IF (EXP5.GT.EX) GO TO 263                                                 573.000
  0023              TERM5=(XNN(5)/DEXP(EXP5))/(1.+CC5*DEXP(EXP5))                             574.000
  0024              GO TO 264                                                                 575.000
  0025         263  TERM5=0.0                                                                 576.000
  0026         264  IF (EXP6.GT.EX) GO TO 265                                                 578.000
  0027              TERM6=(XNN(6)/DEXP(EXP6))/(1.+CC6*DEXP(EXP6))                             579.000
  0028              GO TO 266                                                                 580.000
  0029         265  TERM6=0.0                                                                 581.000
  0030         266  CONTINUE                                                                  582.000
  0031              PRCAL=TR/(ZC*YY(1))+SUM+TERM5+TERM6+TERM7                                 583.000
  0032              DEV=PR-PRCAL                                                              584.000
  0033              PCD=(DEV*100.)/PR                                                         585.000
  0034              RETURN                                                                    586.000
  0035              END                                                                       587.000
   *OPTIONS IN EFFECT*  ID,EBCDIC,SOURCE,NOLIST,NODECK,LOAD,NOMAP
   *OPTIONS IN EFFECT*  NAME = PRESOR   , LINECNT =       57
   *STATISTICS*    SOURCE STATEMENTS =        35,PROGRAM SIZE =     1306
   *STATISTICS*  NO DIAGNOSTICS GENERATED
NO ERRORS IN PRESOR
```

```
MICHIGAN TERMINAL SYSTEM FORTRAN G(41336)              DPDT              01-05-73          20:10.46          PAGE P001

  0001                 SUBROUTINE DPDT (VR,TR,SLOPE)                                                  588.000
  0002                 IMPLICIT REAL*8(A-H,O-Z,$)                                                     589.000
  0003                 COMMON A(10),B(10),C(10),AE5,CC5,AE6,CC6,EX,BAA,R,ZC,AK                        590.000
  0004                 DIMENSION YY(5),ZCC(5)                                                         591.000
  0005                 YY(1)=VR-BAA                                                                   592.000
  0006                 YY(2)=YY(1)*YY(1)                                                              593.000
  0007                 YY(3)=YY(2)*YY(1)                                                              594.000
  0008                 YY(4)=YY(3)*YY(1)                                                              595.000
  0009                 EXP5=AE5*VR                                                                    596.000
  0010                 EXP6=AE6*VR                                                                    597.000
  0011                 ZCC(2)=ZC*ZC                                                                   598.000
  0012                 ZCC(3)=ZCC(2)*ZC                                                               599.000
  0013                 ZCC(4)=ZCC(3)*ZC                                                               600.000
  0014                 AKTR=-AK*TR                                                                    601.000
  0015                 XX=AK*DEXP(AKTR)                                                               602.000
  0016                 SUM=0.0                                                                        603.000
  0017                 DO 271 J=2,4                                                                   604.000
  0018                 XXX=(B(J)-C(J)*XX)/(YY(J)*ZCC(J))                                              605.000
  0019            271  SUM=SUM+XXX                                                                    606.000
  0020                 IF (EXP5.GT.EX) GO TO 272                                                      607.000
  0021                 TERM5=((B(5)-C(5)*XX)/DEXP(EXP5))/(1.+CC5*DEXP(EXP5))                          608.000
  0022                 GO TO 273                                                                      609.000
  0023            272  TERM5=0.0                                                                      610.000
  0024            273  IF (EXP6.GT.EX) GO TO 274                                                      611.000
  0025                 TERM6=((B(6)-C(6)*XX)/DEXP(EXP6))/(1.+CC6*DEXP(EXP6))                          612.000
  0026                 GO TO 275                                                                      613.000
  0027            274  TERM6=0.0                                                                      614.000
  0028            275  CONTINUE                                                                       615.000
  0029                 SLOPE=1./(ZC*YY(1))+SUM+TEPM5+TERM6+TERM7                                      616.000
  0030                 RETURN                                                                         617.000
  0031                 END                                                                            618.000
   *OPTIONS IN EFFECT*  ID,EBCDIC,SOURCE,NOLIST,NODECK,LOAD,NOMAP
   *OPTIONS IN EFFECT*  NAME = DPDT    , LINECNT =       57
   *STATISTICS*    SOURCE STATEMENTS =       31,PROGRAM SIZE =     1094
   *STATISTICS*  NO DIAGNOSTICS GENERATED
NO ERRORS IN DPDT
```

```
MICHIGAN TERMINAL SYSTEM FORTRAN G(41336)             D2PDT2          01-05-73          20:10.47          PAGE P001

  0001              SUBROUTINE D2PDT2 (VR,TR,SLOPE2)                                                     619.000
  0002              IMPLICIT REAL*8(A-H,O-Z,$)                                                           620.000
  0003              COMMON A(10),B(10),C(10),AE5,CC5,AE6,CC6,EX,BAA,R,ZC,AK                              621.000
  0004              VI1=VR-BAA                                                                           622.000
  0005              VI2=VI1*VI1                                                                          623.000
  0006              VI3=VI2*VI1                                                                          624.000
  0007              VI4=VI3*VI1                                                                          625.000
  0008              ZC2=ZC*ZC                                                                            626.000
  0009              ZC3= ZC2*ZC                                                                          627.000
  0010              ZC4=ZC3*ZC                                                                           628.000
  0011              EXP5=AE5*VR                                                                          629.000
  0012              EXP6=AE6*VR                                                                          630.000
  0013              AKTR=-AK*TR                                                                          631.000
  0014              XX=AK*AK*DEXP(AKTR)                                                                  632.000
  0015              IF (EXP5.GT.EX) GO TO 281                                                            633.000
  0016              TERM5=(C(5)/DEXP(EXP5))/(1.+CC5*DEXP(EXP5))                                          634.000
  0017              GO TO 282                                                                            635.000
  0018         281  TERM5=0.0                                                                            636.000
  0019         282  IF (EXP6.GT.EX) GO TO 283                                                            637.000
  0020              TERM6=(C(6)/DEXP(EXP6))/(1.+CC6*DEXP(EXP6))                                          638.000
  0021              GO TO 284                                                                            639.000
  0022         283  TERM6=0.0                                                                            640.000
  0023         284  CONTINUE                                                                             641.000
  0024              SLOPE2=C(2)/(ZC2*VI2)+C(3)/(ZC3*VI3)+C(4)/(ZC4*VI4)                                  642.000
  0025              SLOPE2=XX*SLOPE2                                                                     643.000
  0026              RETURN                                                                               644.000
  0027              END                                                                                  645.000
   *OPTIONS IN EFFECT*  ID,EBCDIC,SOURCE,NOLIST,NODECK,LOAD,NOMAP
   *OPTIONS IN EFFECT*  NAME = D2PDT2  , LINECNT =        57
   *STATISTICS*    SOURCE STATEMENTS =        27,PROGRAM SIZE =       922
   *STATISTICS*  NO DIAGNOSTICS GENERATED
NO ERRORS IN D2PDT2
```

```
MICHIGAN TERMINAL SYSTEM FORTRAN G(41336)             DEVIAN          01-05-73          20:10.48          PAGE P001

   0001               SUBROUTINE DEVIAN (PCDEV,N,AVPCD,ABPCD,STPCD)                           646.000
   0002               IMPLICIT REAL*8(A-H,O-Z,$)                                               647.000
   0003               DIMENSION PCDEV(200)                                                     648.000
   0004               SUM1=0.0                                                                 649.000
   0005               SUM2=0.0                                                                 650.000
   0006               SUM3=0.0                                                                 651.000
   0007               DO 161 I=1,N                                                             652.000
   0008               SUM1=SUM1+PCDEV(I)                                                       653.000
   0009               XX=PCDEV(I)                                                              654.000
   0010               TERM=DABS(XX)                                                            655.000
   0011               SUM2=SUM2+TERM                                                           656.000
   0012               XXX=XX*XX                                                                657.000
   0013               SUM3=SUM3+XXX                                                            658.000
   0014           161 CONTINUE                                                                 659.000
   0015               AVPCD=SUM1/N                                                             660.000
   0016               ABPCD=SUM2/N                                                             661.000
   0017               TERM=SUM3/(N-1)                                                          662.000
   0018               STPCD=DSQRT(TERM)                                                        663.000
   0019               RETURN                                                                   664.000
   0020               END                                                                      665.000
   *OPTIONS IN EFFECT*  ID,EBCDIC,SOURCE,NOLIST,NODECK,LOAD,NOMAP
   *OPTIONS IN EFFECT*  NAME = DEVIAN   , LINECNT =       57
   *STATISTICS*    SOURCE STATEMENTS =       20,PROGRAM SIZE =      716
   *STATISTICS*  NO DIAGNOSTICS GENERATED
 NO ERRORS IN DEVIAN

 NO STATEMENTS FLAGGED IN THE ABOVE COMPILATIONS.
```

```
******* INPUT  DATA  TO  SOLVE  COEFFICIENTS  IN   THE  REDUCED  EQUATION  OF  STATE  **
         TC  =      664.50        VC  =   0.030525        PC  =     721.906
         AK  =        3.00        R   =   0.124098        ZCV =      0.2790
         CC5=         0.00        AE5=  16.000000         ALGF5=    9.706000
         CC6=         0.00        AE6=  22.000000         ALGF6=   11.237700
         TTR=         0.80  ,  BT  =    -0.7400      TTR=        2.30     BT  =     0.0
                                  ROR=   0.666670         SLP1  =   3.91
                                  RCR=   1.400000         SLP1  =  14.10
         TTR=         1.00        ROR=   1.000000         SLP1  =   7.40
         TTR=         1.00        ROR=   1.800000         SLP1  =  23.80
         TTR=         1.00        RCR=   1.000000         SLP2  =   0.0
         TTR=         1.00        ROR=   1.800000         SLP2  =   0.0
```

```
.10000 010.0           0.0         0.0         0.1000D 010.0           0.0         0.0         0.4979D-010.0           0.5250D-01
.0         0.10000 010.0           0.0         0.0         0.10000 010.0           0.0         0.0         0.4979D-01-.3906D-02
.0         0.0         0.10000 010.0           0.0         0.0         0.10000 010.0           0.0         0.0         0.1642D 05
.0         0.0         0.0         0.1000D 010.0           0.0         0.0         0.1000D 010.0           0.0         0.7594D 05
.0         0.0         0.0         0.0         0.1945D 020.5231D 020.4073D-150.1551D-22-.6990D-76-.6990D-760.1092D 00
.0         0.0         0.0         0.0         0.2338D 030.1456D 040.8232D-050.1447D-07-.6990D-76-.6990D-760.2059D 01
.0         0.0         0.0         0.0         0.7357D 020.3105D 030.3506D-080.5557D-13-.1105D 02-.4638D 02-.5361D 01
.0         0.0         0.0         0.0         0.5866D 030.4911D 040.1345D-030.3830D-05-.8762D 02-.7335D 03-.1868D 02
.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.3314D 020.1591D 030.1757D 02
.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.2629D 020.2200D 040.6966D 02
```

```
******  COEFFICIENTS  IN  THE  REDUCED  EQUATION  OF STATE  *******
 ******  PR=TR/(ZC*(VR-B/VC))+(A2+B2*TR+C2*EXP(-K*TR))/(ZC2*(VR-B/VC)*(VR-B/VC))+.....+(A5+B5*TR)/(EXP(AE5*VR))*(1.+CC5*EXP(AE5*VR)
(A6+B6*TR)/(EXP(AE6*VR)*(1.+CC6*EXP(AE6*VR))) ***
                     IE=   0
                     IE=   0
                     A(2)= -.417902D 00
                     B(2)= 0.153671D 00
                     C(2)= -.222487D 01
                     A(3)= 0.191762D-01
                     B(3)= 0.370338D-02
                     C(3)= 0.795797D 00
                     A(4)= -.146404D-02
                     B(4)= 0.710054D-03
                     C(4)= -.633150D-01
                     A(5)= -.357334D 04
                     B(5)= 0.199891D 05
                     A(6)= 0.103874D 07
                     B(6)= -.952803D 06
                     ZC   =       0.267225
                     BAA  =       0.108523
```

```
***** RECALCULATION OF  INPUT  CONDITIONS ****
               TEMP=      664.50     F(TC)= 0.6250D-01     FCAL= 0.6250D-01
               TEMP=      664.50     F(TC)= -.3906D-02     FCAL= -.3906D-02
               TEMP=      664.50     F(TC)= 0.1642D 05     FCAL= 0.1642D 05
               TEMP=      664.50     F(TC)= 0.7594D 05     FCAL= 0.7594D 05
                                     VCL=   1.499993     SLOPE=        3.91     SLPCAL=        3.91
                                     VCL=   0.714286     SLOPE=       14.10     SLPCAL=       14.10
               TEMP=        1.00     VCL=   1.000000     SLOPE=        7.40     SLPCAL=        7.40
               TEMP=        1.00     VOL=   0.555556     SLOPE=       23.80     SLPCAL=       23.80
               TEMP=        0.80     B   =   -0.7400     BCAL=    -0.7400
               TEMP=        2.30     B   =    0.0        BCAL=    -0.0000
               TEMP=        1.00     B   =   -0.3460     BCAL=    -0.3460
               TEMP=        1.00     VCL=   1.000000     SL2=       0.0      SL2CAL=       0.00
               TEMP=        1.00     VOL=   0.555556     SL2=       0.0      SL2CAL=       0.00
```

```
*****  LINEARITY   TESTING  **********
        1.499993        20.000         75.474         75.474       0.0          0.0
        1.499993        21.000         79.384         79.384      -0.000       -0.00
        1.499993        22.000         83.294         83.294      -0.000       -0.00
        0.714286        20.000        268.426        268.426       0.0          0.0
        0.714286        21.000        282.526        282.526      -0.000       -0.00
        0.714286        22.000        296.626        296.626      -0.000       -0.00
        1.000000         1.000          1.000          1.000       0.0          0.0
        1.000000         1.100          1.740          1.740      -0.000       -0.00
        1.000000         1.200          2.480          2.480      -0.000       -0.00
        0.555556         1.000          2.073          2.073       0.0          0.0
        0.555556         1.100          4.453          4.453       0.000        0.00
        0.555556         1.200          6.833          6.833      -0.000       -0.00
```

APPENDIX G

ALGEBRAIC CORRELATION OF VAPOR PRESSURE DATA

All of the experimental vapor pressure data has been correlated by the Martin, Kapoor and Shinn equation (93) which is given by the following expression:

$$\ln P = A + \frac{B}{T} + C\ln T + DT + \frac{E(F-T)}{FT} \ln(F-T) \qquad \text{(G-1)}$$

There are six unknowns in Equation (G-1), namely, A,B,C,D,E and F. In the process of evaluating these parameters, the first step is to assume $F = 1.02\ T_c$. Here we shall illustrate the data fitting process with respect to vapor pressure values of R-115. All of the experimental vapor pressure data of R-115 is given in Figure V- 4 . Given the critical temperature of R-115 to be 635.56 R, we obtain:

$$F = 1.02\ T_c = 648.27 \qquad \text{(G-2)}$$

Then five points from Fig. V-4 are selected and substituted in Equation (G-1) to obtain five simultaneous equations which can be solved for the remaining unknowns. The five points on the vapor pressure plot (Fig. V-4) selected for R-115 are given in Table G-1.

TABLE G-1

Five Points on the Vapor Pressure Plot for R-115 (Fig. V-4) Selected to Solve Unknowns in Eqn. (G-1)

$\frac{1}{T}\times 10^3$ $(R)^{-1}$	T R	P psia
3.0	333.33	0.82
2.5	400.00	8.3
2.1	476.19	48.2
1.8	555.56	173.0
1.6	625.00	406.0

Solving five simultaneous equations of the type (Equation G-1) the parameters for R-115 are as follows.

Result

$A = 80.727001$

$B = -7885.8583$

$C = -10.497278$

$D = 0.00873321$

$E = 95.588673$

$F = 648.27$

Computer Program to Correlate Vapor Pressure Data of R-115 with Eqn. (G-1)

```
MICHIGAN TERMINAL SYSTEM FORTRAN G(41336)          MAIN          02-03-73          19:29.48          PAGE P001

           C    ******     CALCULATIONS OF CONSTANTS OF VAPOR PRESSURE EQUATION                       5.000
  0001                IMPLICIT REAL*8(A-H,O-Z,$)                                                       6.000
  0002                DIMENSION A(5,5),B(5),T(50),P(50),PP(50)                                         7.000
  0003                TC=635.56                                                                        8.000
  0004                PC=456.0                                                                         9.000
  0005                I=0.0                                                                           10.000
  0006           11   I=I+1                                                                           11.000
  0007                N=I                                                                             12.000
  0008                READ (5,100,END=12) T(I),P(I)                                                   13.000
  0009                X11=T(I)-1000.                                                                  14.000
  0010                X1=DABS(X11)                                                                    15.000
  0011                IF (X1.LT.0.1) GO TO 12                                                         16.000
  0012                GO TO 11                                                                        17.000
  0013          100   FORMAT (2F15.3)                                                                 18.000
  0014          101   FORMAT (2F15.3,1I1)                                                             19.000
  0015           50   FORMAT ('1',/)                                                                  20.000
  0016           51   FORMAT ('                              TEMP           PEXP             PC         21.000
                     1AL          PCD        I')                                                      22.000
  0017           12   CONTINUE                                                                        23.000
  0018                F=648.27                                                                        24.000
  0019                DO 13 I=1,5                                                                     25.000
  0020                A(I,1)=1.0                                                                      26.000
  0021                A(I,2)=1./T(I)                                                                  27.000
  0022                A(I,3)=DLOG(T(I))                                                               28.000
  0023                A(I,4)=T(I)                                                                     29.000
  0024                FTI=F-T(I)                                                                      30.000
  0025                A(I,5)=(FTI*DLOG(FTI))/(F*T(I))                                                 31.000
  0026           13   B(I)=DLOG(P(I))                                                                 32.000
  0027                CALL DGELG(B,A,5,1,1.E-15,IER)                                                  33.000
  0028                AA=B(1)                                                                         34.000
  0029                BB=B(2)                                                                         35.000
  0030                CC=B(3)                                                                         36.000
  0031                DD=B(4)                                                                         37.000
  0032                EE=B(5)                                                                         38.000
  0033                FF=F                                                                            39.000
  0034                AA=80.727001                                                                    40.000
  0035                BB=-7885.8583                                                                   41.000
  0036                CC=-10.497278                                                                   42.000
  0037                DD=0.0087332099                                                                 43.000
  0038                EE=95.588673                                                                    44.000
           C    ******     PRINT AA,BB,CC,DD,EE,FF                                                    45.000
  0039                WRITE (6,50)                                                                    46.000
  0040                WRITE (6,200) IER                                                               47.000
  0041                WRITE (6,201) AA                                                                48.000
  0042                WRITE (6,202) BB                                                                49.000
  0043                WRITE (6,203) CC                                                                50.000
  0044                WRITE (6,204) DD                                                                51.000
  0045                WRITE (6,205) EE                                                                52.000
  0046                WRITE (6,206) FF                                                                53.000
  0047          200   FORMAT('0',20X,'IER= ',I2)                                                      54.000
  0048          201   FORMAT ('0',20X,'AA= ',E15.8)                                                   55.000
  0049          202   FORMAT ('0',20X,'BB= ',E15.8)                                                   56.000
  0050          203   FORMAT ('0',20X,'CC= ',E15.8)                                                   57.000
  0051          204   FORMAT ('0',20X,'DD= ',E15.8)                                                   58.000
  0052          205   FORMAT ('0',20X,'EE= ',E15.8)                                                   59.000
```

```
MICHIGAN TERMINAL SYSTEM FORTRAN G(41336)          MAIN           02-03-73        19:29.48        PAGE P002

  0053          206  FORMAT ('0',20X,'FF= ',E15.8)                                                    60.000
               C    ******    COMPARISON OF THE DATA                                                  61.000
               C    ******  INPUT UNITS ARE:                                                          62.000
               C    ******  TEMPERATURE IN DEGREES FAHRENHEIT                                         63.000
               C    ******  PRESSURE IN PSIA                                                          64.000
               C    ******  IER IS THE REFERENCE NUMBER AS:                                           65.000
               C    ******  IER=1  REFERS    UNIVERSITY OF MICHIGAN                                   66.000
               C    ******  IER=2  REFERS    MEAR ET.AL                                               67.000
               C    ******  IER=3  REFERS    ASTON                                                    68.000
               C    ******  IER=4  REFERS    DU PONT X-57 B                                           69.000
  0054                N=N-1                                                                           70.000
  0055                DO 14 I=1,N                                                                     71.000
  0056                FTI=F-T(I)                                                                      72.000
  0057                DLOGP=AA+BB/T(I)+CC*DLOG(T(I))+DD*T(I)+(EE*FTI*DLOG(FTI))/(F*T(I))              73.000
  0058                PP(I)=DEXP(DLOGP)                                                               74.000
  0059                DEV=P(I)-PP(I)                                                                  75.000
  0060                PCD=DEV*100./P(I)                                                               76.000
  0061            14  WRITE (6,300) T(I),P(I),PP(I),PCD                                               77.000
  0062           300  FORMAT ('0',20X,F10.2,2F15.4,F10.2)                                             78.000
  0063            10  WRITE (6,50)                                                                    79.000
  0064                WRITE (6,51)                                                                    80.000
  0065            15  READ (5,101) TEMP,PEXP,IER                                                      81.000
  0066                X12=TEMP-2000.                                                                  82.000
  0067                X13=TEMP-3000.                                                                  83.000
  0068                X14=TEMP-4000.                                                                  84.000
  0069                X15=TEMP-5000.                                                                  85.000
  0070                X2=DABS(X12)                                                                    86.000
  0071                X3=DABS(X13)                                                                    87.000
  0072                X4=DABS(X14)                                                                    88.000
  0073                X5=DABS(X15)                                                                    89.000
  0074                IF (X2.LT.0.1) GO TO 10                                                         90.000
  0075                IF (X3.LT.0.1) GO TO 10                                                         91.000
  0076                IF (X4.LT.0.1) GO TO 10                                                         92.000
  0077                IF (X5.LT.0.1) GO TO 10                                                         93.000
  0078                TT=TEMP+459.67                                                                  94.000
  0079                RHS=AA+BB/TT+CC*DLOG(TT)+DD*TT+(EE*(FF-TT)/(FF*TT))*(DLOG(FF-TT))               95.000
  0080                PCAL=DEXP(RHS)                                                                  96.000
  0081                DEV=PEXP-PCAL                                                                   97.000
  0082                PCD=DEV*100./PEXP                                                               98.000
  0083                WRITE (6,400) TEMP,PEXP,PCAL,PCD,IER                                            99.000
  0084                GO TO 15                                                                       100.000
  0085           400  FORMAT ('0',20X,F10.2,2F15.4,F10.2,5X,I1)                                      101.000
  0086                END                                                                            102.000
   *OPTIONS IN EFFECT*  ID,EBCDIC,SOURCE,NOLIST,NODECK,LOAD,NOMAP
   *OPTIONS IN EFFECT*  NAME = MAIN     , LINECNT =        57
   *STATISTICS*    SOURCE STATEMENTS =          86,PROGRAM SIZE =       3912
   *STATISTICS*  NO DIAGNOSTICS GENERATED
NO ERRORS IN MAIN

NO STATEMENTS FLAGGED IN THE ABOVE COMPILATIONS.
```

APPENDIX H

ALGEBRAIC CORRELATION OF SATURATED LIQUID DENSITY DATA

All of the experimental saturated liquid density data has been correlated by the Hou equation (62). The equation is as follows:

$$d_s = A + B(1-T_R)^{1/3} + C(1-T_R)^{2/3} + D(1-T_R)^{4/3} \qquad \text{(H-1)}$$

The form of the equation requires that $A = d_c$. The other four unknowns B,C,D, and E are evaluated by choosing four saturated liquid density values. The method of evaluating these constants is illustrated for R-115.

All the experimental saturated liquid density data for R-115 is given in Fig. IV-2. Four saturated density values for R-115 are selected from Fig. IV-2 which are given in Table H-1.

TABLE H-1

Four Points on the Saturated Liquid Density Plot for R-115 (Fig. V-6) Selected to Solve Unknowns in Eqn. (H-1)

t F	ds lbs/cu.ft.
-150	108.98
30	87.7
130	69.45
150	63.3

The result of the solution of four simultaneous equations is as follows:

A = 37.3

B = 65.70716

C = 39.788587

D = -47.381529

E = 43.599542

Computer Program to Correlate Saturated Liquid Density Data of R-115 with Eqn. (H-1)

```
MICHIGAN TERMINAL SYSTEM FORTRAN G(41336)          MAIN          02-03-73          20:21.22          PAGE P001

      C     ******    CALCULATIONS OF CONSTANTS OF SATURATED LIQUID DENSITY
      C EQUATION
            IMPLICIT REAL*8(A-H,O-Z,$)
            DIMENSION  A(4,4),B(4),T(30),DS(30),DSS(30)
            TC=635.56
            AA=37.3
            I=0.0
         11 I=I+1
            N=I
            READ (5,100,END=12) T(I),DS(I)
            X11=1000.-T(I)
            IF (X11 .LT.0.1) GO TO 12
            T(I)=T(I)+459.67
            GO TO 11
         12 DO 13 I=1,4
            X=1.-T(I)/TC
            XX=X**(1./3.)
            A(I,1)=XX
            A(I,2)=XX**2.
            A(I,3)=XX**3.
            A(I,4)=XX**4.
         13 B(I)=DS(I) -AA
            CALL DGELG(B,A,4,1,1.E-15,IER)
            BB=B(1)
            CC=B(2)
            DD=B(3)
            EE=B(4)
            N=N-1
      C    *****   PRINT AA,BB,CC,DD,EE,
            WRITE (6,50)
            WRITE (6,200) IER
            WRITE (6,201) AA
            WRITE (6,202) BB
            WRITE (6,203) CC
            WRITE (6,204) DD
            WRITE (6,205) EE
         50 FORMAT ('1',/)
        200 FORMAT ('0',20X,'IER= ',I2)
        201 FORMAT ('0',20X,'AA= ',E15.8)
        202 FORMAT ('0',20X,'BB= ',E15.8)
        203 FORMAT ('0',20X,'CC= ',E15.8)
        204 FORMAT ('0',20X,'DD= ',E15.8)
        205 FORMAT ('0',20X,'EE= ',E15.8)
      C    ******     COMPARISON OF THE DATA
            DO 14 I=1,N
            X=1.-T(I)/TC
            XX=X**(1./3.)
            DSS(I)=AA+BB*XX+CC*(XX**2.)+DD*(XX**3.)+EE*(XX**4.)
            DEV=DS(I)-DSS(I)
            PCD=DEV*100./DS(I)
         14 WRITE (6,300) T(I),DS(I),DSS(I),PCD
        100 FORMAT (2F15.3)
        300 FORMAT ('0',20X,F12.2,2F15.3,F12.2)
      C     *****    INPUT UNITS ARE:
      C     *****    TEMPERATURE IN DEGREES FAHRENHEIT
```

```
MICHIGAN TERMINAL SYSTEM FORTRAN G(41336)            MAIN            02-03-73          20:21.22          PAGE P002
               C    *****   DENSITY IN POUNDS PER CUBIC FOOT                                        59.000
               C    *****   IER IS THE REFERENCE NUMBER AS:                                         60.000
               C   ******  IER=1  REFERS    UNIVERSITY OF MICHIGAN                                  61.000
               C   ******  IER=2  REFERS    MEARS ET AL                                             62.000
  0050          10  WRITE (6,50)                                                                    63.000
  0051          15  READ (5,101) TEMP,DEXP,IER                                                      64.000
  0052              X12=2000.-TEMP                                                                  65.000
  0053              X13=3000.-TEMP                                                                  66.000
  0054              X14=4000.-TEMP                                                                  67.000
  0055              IF (X12 .LT.0.1) GO TO 10                                                       68.000
  0056              IF (X13 .LT.0.1) GO TO 10                                                       69.000
  0057              IF (X14 .LT.0.1) GO TO 10                                                       70.000
  0058              TT=TEMP+459.67                                                                  71.000
  0059              X=1.-TT/TC                                                                      72.000
  0060              Y=1./3.                                                                         73.000
  0061              XX=X**Y                                                                         74.000
  0062              DCAL=AA+BB*XX+CC*(XX**2.)+DD*(XX**3.)+EE*(XX**4.)                               75.000
  0063              DEV=DEXP-DCAL                                                                   76.000
  0064              PCD=DEV*100./DEXP                                                               77.000
  0065              WRITE (6,301) TEMP,DEXP,DCAL,PCD,IER                                            78.000
  0066              GO TO 15                                                                        79.000
  0067         101  FORMAT (2F15.3,I1)                                                              80.000
  0068         301  FORMAT ('0',10X,F12.2,2F12.3,F12.2,5X,1I1)                                      81.000
  0069              END                                                                             82.000
  *OPTIONS IN EFFECT*  ID,EBCDIC,SOURCE,NOLIST,NODECK,LOAD,NOMAP
  *OPTIONS IN EFFECT*  NAME = MAIN    , LINECNT =       57
  *STATISTICS*    SOURCE STATEMENTS =       69,PROGRAM SIZE =      3000
  *STATISTICS*  NO DIAGNOSTICS GENERATED
NO ERRORS IN MAIN

NO STATEMENTS FLAGGED IN THE ABOVE COMPILATIONS.
```

APPENDIX J

MIXING RULES FOR CRITICAL CONSTANTS

Several mixing rules are given in the literature to predict either pseudocritical or true critical values of a mixture. Some rules are given by Reid and Sherwood (120). The latest summary of the rules to predict true critical values is given by Spencer, Daubert and Danner (130a). In the following analysis a few simple rules along with highly recommended ones are discussed.

For the calculations, several component properties were used and they are given in Table J-1 along with the same properties for mixture.

TABLE J-1

Properties of Components and the Mixture R-502

Property	Units	R-22	R-115	R-502
P_c	psia	721.906	456.0	591.0
T_c	R	664.5	635.56	639.56
V_c	ft^3/lb	0.030525	0.02681	0.028571
Z_c		0.2672	0.2769	0.2747
$T_{B.P.}$	R	418.33	421.99	409.92
ω		0.226	0.2645	0.218
Mol.Wt.		86.476	154.48	111.641
x		0.488	0.512	-
y		0.630	0.370	-
R	$(psia)(ft^3)/(lb)(R)$	0.124098	0.069468	0.0961248

where P_c = critical pressure

T_c = critical temperature

V_c = critical volume

Z_c = critical compressibility factor

$T_{B.P.}$ = normal boiling point

ω = accentric factor

x = mass fraction

y = mole fraction

R = gas constant

G = property denoted generally

(I) Kay's Rule - Mole Fraction

$P_{cm} = 0.63(721.906) + 0.37\ (456) = 623.52$ psia

$T_{cm} = 0.63(664.5) + 0.37\ (635.56) = 653.8$ R

$V_{cm} = 0.63(0.030525)(86.476) + 0.37\ (0.02681(154.48)$

$= 3.1954$ ft^3/lb mole $= 0.028622$ ft^3/lb

$Z_{cm} = 0.63(0.2672) + 0.37\ (0.2769) = 0.2705$

(II) Kay's Rule - Mass fraction

$P_{cm} = 0.488(721.906) + 0.512(456.0) = 585.76$ psia

$T_{cm} = 0.488(644.5) + 0.512(635.56) = 649.69$ R

$V_{cm} = 0.488\ (0.030525 + 0.512(0.02681)$

$= 0.028622$ ft^{3}lb

$Z_{cm} = 0.488(0.2672) + 0.512(0.2769) = 0.2821$

(III) Geometric mean averages

$$G_{mix} = (y_A G_A^{1/2} + y_B G_B^{1/2}) \qquad \text{(J-1)}$$

$P_{cm} = 616.4$ psia

$T_{cm} = 653.0$ R

$V_{cm} = 0.63(2.63968)^{1/2} + 0.37(4.14161)^{1/2} = 3.157$ ft^3/lb mole

$= 0.0283$ ft^3/lb

$Z_{cm} = 0.272$

(IV) Lorentz cube root averages

$$G_{mix} = y_A^2 G_A + \frac{y_A y_B}{4} (G_A^{1/3} + G_B^{1/3})^3 + y_B^2 G_B \qquad \text{(J-2)}$$

$P_{cm} = 617.0$ psia

$T_{cm} = 655.0$ R

$V_{cm} = 0.0284$ ft^3/lb

$Z_{cm} = 0.2705$

(V) Chueh and Prausnitz (34a):

$$V_{cm} = \Sigma\, y_i\, V_{ci} = 0.028622 \text{ ft}^3\text{/lb} \qquad \text{(J-3)}$$

$$T_{cm} = \Sigma\, \Sigma \quad \phi_i \phi_j\, T_{cij} \qquad \text{(J-4)}$$

where

$$\phi_i = \frac{y_i V_{ci}}{\Sigma y_i V_{ci}}$$

and

$$T_{cij} = (T_{ci} T_{cj})^{1/2} (1-k_{ij}) \qquad \text{(J-5)}$$

where

$$k_{ij} = 1 - \left[\frac{(V_{ci}^{1/3} V_{cj}^{1/3})^{0.5}}{(V_{ci}^{1/3}+V_{cj}^{1/3})/2}\right]^3$$

$\phi_1 = 0.5204$

$\phi_2 = 0.4796$

$k_{ij} = 0.00841$

$T_{cij} = 644.4$ R

$T_{cm} = 647.81$ R

(VI) Chueh and Prausnitz (34b):

$$V_{cm} = \Sigma\ \theta_i V_{ci} + \Sigma\ \Sigma\ \theta_1 \theta_j V_{ij} \qquad \text{(J-6)}$$

$$T_{cm} = \Sigma\ \theta_i\ T_{ci} + \Sigma\Sigma\ \theta_1 \theta_j\ T_{ij} \qquad \text{(J-7)}$$

where

$$\theta_i = \frac{y_i V_{ci}^{2/3}}{y_i V_{ci}^{2/3}}$$

$T_{ii} = 0$

$V_{ii} = 0$

$\theta_1 = 0.56$

$\theta_2 = 0.44$

$$\frac{T_{c1}-T_{c2}}{T_{c1}+T_{c2}} = 0.02226$$

$T_{ij} = 0$

$T_{cm} = 652.1$ R

$V_{cm} = 0.0296$ ft^3/lb

(VII) Ekiner and Thodos (479):

$$T_c - T'_c = A_{ij} y_i + (B_{ij} - A_{ij})\, y_i^2 - B_{ij} y_i^3 \tag{J-8}$$

where $T'_c = y_i T_{ci}$

$$A_{ij} = e^{[6.048\ (T_{ij}-1)^{1/3}-1]}$$

$$B_{ij} = e^{[6.356\ (T_{ij}-1)^{1/4}-1]}$$

$$T_{ij} = \frac{T_{ci}/M_i}{T_{cj}/M_j} > 1$$

$\therefore\ T_c - T'_c = 5.3$ R

$T_c = 5.3 + 653.8 = 659.1$

(VIII) Grieves and Thodos (52a):

$$T_{cm} = \frac{T_{c1}}{1 + \frac{y_2}{y_1} A_{12}} + \frac{T_{c2}}{1 + \frac{y_1}{y_2} A_{21}} \tag{J-9}$$

where A_{12} and A_{21} are functions of $\frac{T_{b2}}{T_{b1}} > 1$

$$\therefore \frac{T_{b2}}{T_{b1}} = 1.0087$$

$$A_{21} = 0.8$$

$$A_{12} = 1.2$$

$$T_{cm} = 650.78 \text{ R}$$

(IX) Leland-Mueller (84a):

$$T_{cm} = \frac{[\Sigma\, y_i (Z_{ci}\, R\, T_{ci}^{\alpha+1}/P_{ci})^{1/2}]^{2 \quad 1/\alpha}}{V_{cm}} \tag{J-10}$$

where $V_{cm} = \frac{1}{8}\ \Sigma\Sigma\ y_i y_i\ [V_{ci}^{1/3} + V_{cj}^{1/3}]^3$

$$Z_{cm} = \Sigma\ y_i Z_{ci}$$

$$\alpha = 2.43 - 0.74\,\theta \qquad 1.9 > \theta > 0.5$$

$$= 2.2 \qquad \theta < 0.5$$

$$= 1.0 \qquad \theta > 1.9$$

$$\theta = \frac{P}{T}\ \frac{T_{cm}(K)}{P_{cm}(K)}$$

$$T_{cm}(K) = \Sigma\ y_i T_{ci}$$

$$P_{cm}(K) = \Sigma\ y_i P_{ci}$$

$$P_{cm} = RT_{cm}\ Z_{cm}/V_{cm} \tag{J-11}$$

Values are:

= 1.72

$V_{cm} = 0.028388 \text{ ft}^3/\text{lb}$

$T_{cm} = 655.0 \text{ R}$

$Z_{cm} = 0.2705$

$P_{cm} = 600.0 \text{ psia}$

(X) Joffe-Method A (67a):

$$\frac{T_{cm}}{P_{cm}^{1/2}} = y_1 \frac{T_{c1}}{P_{c1}^{1/2}} + y_2 \frac{T_{c2}}{P_{c2}^{1/2}} = K \tag{J-12}$$

$$\frac{T_{cm}}{P_{cm}} = y_1 \frac{T_{c1}}{P_{c1}} + y_2 \frac{T_{c2}}{P_{c2}} = J \tag{J-13}$$

$T_{cm} = K^2/J = 645.53 \text{ R}$

$P_{cm} = T_{cm}/J = 589.2 \text{ psia for } T_{cm} = 645.53 \text{ R}$

$= 583.9 \text{ psia for } T_{cm} = 639.56 \text{ R}$

$P_{cm} = K^2/T_{cm} = 578.6 \text{ psia for } T_{cm} = 639.56 \text{ R}$

(XI) Joffe-Method B (67a):

$$J = \frac{T_{cm}}{P_{cm}} = y_1^2 \frac{T_{c1}}{P_{c1}} + y_2^2 \frac{T_{c2}}{P_{c2}} + \frac{1}{4} \left[\left(\frac{T_u}{P_u}\right)^{1/3} + \left(\frac{T_{c2}}{P_{c2}}\right)^{1/3} \right]^3 y_1 y_2 \tag{J-14}$$

$= 1.0881$

$$T_{cm} = K^2/J = 649.98 \text{ R}$$

$$P_{cm} = T_{cm}/J = 597.35 \text{ psia for } T_{cm} = 649.98 \text{ R}$$

$$= 587.9 \text{ psia for } T_{cm} = 639.56 \text{ R}$$

(XII) Li (85a):

$$T_{cm} = \Sigma \;\; \phi_i T_{ci} \qquad \text{(J-15)}$$

where

$$\phi_i = \frac{y_i V_{ci}}{y_i V_{ci}}$$

$$\phi_1 = 0.5204, \quad T_{c1} = 664.5 \text{ R}$$

$$\phi_2 = 0.4796, \quad T_{c2} = 635.56 \text{ R}$$

$$T_{cm} = 650.6 \text{ R}$$

(XIII) Kreglewski and Kay (82a):

$$P_{cm} = P_{cp} + P_{cp}[5.808 + 4.93 \; (\omega_1 y_1 + \omega_2 y_2)] \; \frac{T_{cm} - T_{cp}}{T_{cp}} \qquad \text{(J-16)}$$

$$\therefore P_{cm} = 623.52 + 623.52 \; [5.808 + 4.93(0.2403)] \; \frac{639.56-653.8}{653.8}$$

$$= 528.56 \text{ psia}$$

(XIV) Li, Chen and Murphy (85b):

$$\frac{T_{bm}}{T_{cm}} = y_1 \frac{T_{b1}}{T_{c1}} + y_2 \frac{T_{b2}}{T_{c2}} \qquad \text{(J-17)}$$

$$\therefore \quad \frac{409.92}{T_{cm}} = (0.63)\,\frac{418.33}{664.5} + (0.37)\,\frac{421.99}{635.56}$$

$$T_{cm} = 638.23 \text{ R}$$

(XV) This work:

$$\frac{1}{P_{cm}} = \frac{y_1}{P_{c1}} + \frac{y_2}{P_{c2}} \qquad \text{(J-18)}$$

$$= \frac{0.63}{721.906} + \frac{0.37}{456.6}$$

$$P_{cm} = 593.79 \text{ psia}$$

APPENDIX K

ANALYTICAL METHOD TO OBTAIN INTERMOLECULAR POTENTIAL ENERGY PARAMETERS

General form of the intermolecular potential energy is given before in Fig. II-8 and reproduced here in Figure K-1.

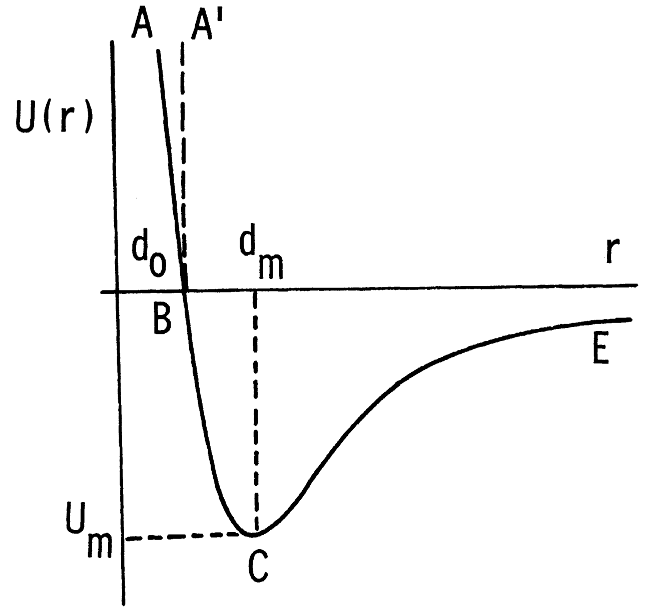

Fig. K-1. General Representation of the Intermolecular Potential Energy

Lennard-Jones (85) described the potential energy by the following equation:

$$U(r) = 4U_m \left[\left(\frac{d_o}{r}\right)^{12} - \left(\frac{d_o}{r}\right)^{6} \right] \tag{K-1}$$

This equation can be substituted in the following equation to obtain the second virial coefficient:

$$B = 2\pi N \int_{o}^{\infty} (e^{-U_m/kT} - 1) r^2 dr \tag{K-2}$$

Resulting expression is given in Eqn. (II-49) which involves two parameters U_m and d_m. The methods of evaluation of these parameters are given by Hirschfelder, Curtiss and Bird (58). These methods are very time consuming.

Here a method is proposed to evaluate these characteristic parameters U_m and d_m analytically. The parameters are calculated for the mixture as well as pure components.

First the potential energy curve is split into positive and negative portion. Then for the positive portion the curve is modified as following A'B rather than AB in the Fig. K-1. Negative portion of the curve is left as before. The total curve is defined analytically by the following two equations:

$$U = -4U_m \left[\left(\frac{d_o}{r}\right)^{12} - \left(\frac{d_o}{r}\right)^{6} \right] \qquad \text{for } d_o < r < \infty \tag{K-3}$$

and

$$e^{-U/kT} = Cr^{12} \qquad \text{for } 0 < r < d_o \tag{K-4}$$

where C is independent of the temperature. From the condition that at $r = d_o$, $U = 0$ we obtain the constant C.

$$C = d_o^{-12} \tag{K-5}$$

Combining Eqns. (K-3), (K-4) and (K-5) with (K-2) we get:

$$B = -2\pi N \int_0^{d_o} \left[\left(\frac{r}{d_o}\right)^{12} - 1 \right] r^2 dr + 2\pi N \int_{d_o}^{\infty} \left(e^{-U/kT} - 1\right) r^2 dr \qquad \text{(K-6)}$$

The magnitude of the term U/kT is not great in the region from d_o to ∞, therefore the following assumption may be made in this region:

$$e^{-U/kT} = 1 - U/kT + 1/2\ (U/kT)^2 \qquad \text{(K-7)}$$

Combining equations (K-6) and (K-7) we get:

$$B = -2\pi N \int_0^{d_o} \left[\left(\frac{r}{d_o}\right)^{12} - 1 \right] r^2 dr - 2\pi N \int_{d_o}^{\infty} \left[-\frac{U}{kT} + \frac{1}{2} \left(\frac{U}{kT}\right)^2 \right] r^2 dr \qquad \text{(K-8)}$$

Integration in Eqn. (K-8) can be carried out to yield the following result:

$$B = 8\pi N d_o^3 \left[\frac{1}{15} + \frac{2}{9} \left(\frac{U_m}{kT}\right) - \frac{16}{315} \left(\frac{U_m}{kT}\right)^2 \right] \qquad \text{(K-9)}$$

Eqn. (K-9) is used in evaluating the parameters d_o and U_m. The calculations are illustrated here for R-22.

Calculation of intermolecular potential parameters

In Eqn. (K-9), it is easier to solve U_m/kT from the fact that at Boyle temperature, B = 0.

$$\therefore \quad \frac{16}{315}\left(\frac{U_m}{kT_B}\right)^2 - \frac{2}{9}\left(\frac{U_m}{kT_B}\right) - \frac{1}{15} = 0 \qquad \text{(K-10)}$$

Root of Eqn. (K-10) is

$$U_m/kT_B = -\ 0.282 \qquad \text{(K-11)}$$

For R-22,

$$T_B = 2.3\ T_c = 849.1\ \text{K}.$$

$$\therefore \quad \frac{U_m}{k} = 0.282\ (849.1)$$

$$\frac{U_m}{k} = -239.3\ \text{K} \qquad \text{(K-12)}$$

To evaluate d_o we must use the following fact:

$$@\ T = T_c = 369.17\ \text{K} \qquad \frac{BP_c}{RT_c} = -0.346 \qquad \text{(K-13)}$$

$$B = -0.346\ \frac{RT_c}{P_c}$$

$$= \frac{(-0.346)(82.06)(369.17)(14.696)}{(721.906)}$$

$$= -213.38\ \text{cc/gmole}$$

Substituting this in Eqn. (K-9) d_o can be obtained

$$-213.38 = 8\ \ (6.023\text{x}10^{23})(d_o{}^3 10^{-24})\left[\frac{1}{15} - \frac{2}{9}\left(\frac{239.3}{369.17}\right)\right.$$

$$\left. - \frac{16}{315}\left(\frac{239.3}{369.17}\right)^2\right]$$

$$\therefore \quad d_o^3 = 14.48$$

$$\therefore \quad d_o = 524 \text{ Å}$$

$$d_m = 2^{1/6}\, d_o = 1.22\, d_o = 5.88\text{Å}$$

$$\therefore \quad \text{For R-22, } d_o = 5.24\text{Å},\ U_m/k = -239.3 \text{ K} \qquad \text{(K-14)}$$

Let us see how these values predict the second virial coefficient at the other condition where

$$@\ T = 0.8\ T_c = 295.33 \text{ K}, \quad \frac{BP_c}{RT} = -0.740$$

or

$$B_{exp} = 365.1 \text{ cc/gmole}$$

Substituting values from (K-14) into (K-9) we get:

$$B = 8\pi(6.023\text{x}10^{23})(5.24)^3 10^{-24} \left[\frac{1}{15} + \frac{2}{9}\left(\frac{-239.3}{295.33}\right) - \frac{16}{315}\left(\frac{-239.3}{295.33}\right)^2\right]$$

$$= -361.0 \text{ cc/gmole compared to } -365.1 \text{ cc/gmole}$$

Proceeding similarly for R-115 we obtain:

$$U_m/K = -288.9 \text{ K}, \quad d_o = 5.98\text{Å}, \quad d_m = 6.71\text{Å} \qquad \text{(K-15)}$$

Intermolecular Potential Parameters for R-502

There are two ways we can calculate the parameters U_m and d_o for R-502. We can assume that it is a pure substance and from generalized second virial coefficient, calculate the parameter or treat it as a mixture. Both approaches are described below.

For R-502:

$$T_c = 355.13 \text{ K}$$

$$T_B = 2.3\ T_c = 817.22 \text{ K} \qquad B = 0$$

$$T_c = 355.31 \text{ K}, \quad \frac{BP_c}{RT} = -0.3425$$

and

$$T_c = 0.8\ T_c = 284.25 \text{ K} \quad \frac{BP_c}{RT} = -0.735 \tag{K-16}$$

Proceeding as before:

$$\text{from } T_B = 817.22 \text{ K}, \qquad \underline{U_m/k = -230.33 \text{ K}} \tag{K-17}$$

and from $-B = 248.4$ cc/gmole, at $T = T_c$

$$\underline{d_o = 5.5\ \mathring{A}} \tag{K-18}$$

Values of U_m/k and d_o from Eqns. (K-17) and (K-18) predict the second virial at $T = 0.8\ T_c$ as follows:

$$B_{calc} = -420.0 \text{ cc/gmole} \tag{K-19}$$

$$B_{exp} = -\frac{(0.735)(82.06)(284.25)(14.7)}{591.0}$$

$$= -425.0 \text{ cc/gmole} \tag{K-20}$$

Thus the second virial coefficient at 0.8 T_c is predicted within 5 cc/gmole which is usually the precision of second virial values.

For a binary mixture the second virial coefficient is:

$$B_{mix} = x_1^2 B_{11} + 2 x_1 x_2 B_{12} + x_2^2 B_{22} \tag{K-21}$$

where B_{mix} = second virial for the mixture

B_{11}, B_{22} = second virial for the components 1 and 2

B_{12} = second virial for the interaction between a molecule of component 1 and component 2

x_1, x_2 = mole fractions of components 1 and 2

Therefore the second virial coefficients of the components must be evaluated at the temperatures at which the mixture second virial coefficients are known. These temperatures are 817.22, 355.31 and 284.25 K. To accomplish this we used the equation of state of R-22 and R-115 as follows:

$$\frac{BP_c}{RT} = \frac{f_2(TR)}{T_R^{\,2}} + \frac{b}{T_R} \tag{K-22}$$

where

$$f_2(T_R) = A_2 + B_2 T_R + C_2 e^{-kT_R}$$

for R-22:

A_2 = -0.417902

B_2 = 0.153671

C_2 = -2.22487

b = 0.029

T_c = 369.17 K

Using Eqn. (K-22),values of second virial coefficients for R-22 are as follows:

T = 817.22 K	B = +4 .578 cc/gmole
T = 355.31 K	B = -234.61 cc/gmole
T = 284.25 K	B = -399.1 cc/gmole (K-23)

For R-115 constants in Eqn. (K-22) are:

A_2 = -0.405920

B_2 = 0.142469

C_2 = -2.24052

b = 0.035

T_c = 353.09 K (K-24)

And we obtain the second virial coefficients as follows:

T = 817.22 K	B = 1.076 cc/gmole
T = 355.31 K	B = 312.54 cc/gmole
T = 284.25 K	B = 537.35 cc/gmole (K-25)

Using these values in Eqn. (K-21), B_{12} can be calculated and the results are summarized in Table K-1.

TABLE K-1

Summary of Second Virial Coefficients of R-22, R-115 and R-502

Second Virial Coefficient cc/gmole

T K	R-22	R-115	R-502	B_{12}	B_{12} calc
817.22	-4.578	+1.076	0.0	+3.58	+3.02
355.31	-234.61	-312.54	-248.3	-241.09	-251.53
284.25	-399.10	-537.35	-425.0	-431.35	-402.3

Using the mixing rule for the intermolecular parameters, we can obtain interaction parameters as follows:

$$d_{o_{12}} = (d_{o_1} + d_{o_2})/2 = 5.61\text{Å}$$

$$U_{m_{12}} = (U_{m_1} U_{m_2})^{1/2} = 234 \text{ cc/gmole} \qquad \text{(K-26)}$$

The parameters given in (K-26) are used in Eqn. (K-9) to predict B_{12} and the results are given in Table K-1. Examination of Table K-1 reveals that the B_{12} predicted is within close agreement with values obtained from the mixture and pure component data.

REFERENCES

1. Aimé, G., Ann. Chim. Phys. 8 257 (1843).
2. Amagat, E.H., Ann. Chim. Phys. 29 68 (1983).
3. American Standards Association.,"Designation of Refrigerants", ASA-B79 (1960).
4. Aston, J.G., Wills, P.E., Zolki, T.P., J. Am. Chen. Soc. 77 3939 (1955).
5. Badylkes, I.S., Bull. Inst. Intern. Froid. Annexe, No. 4, 195 (1965).
6. Badylkes, I.S., Kholodil'n. Tekn. 41(5) 41-6 (1964).
7. Badylkes, I.S., The Journal of Refrigeration, p. 18, Jan. 1966.
8. Beattie, J.A., Proc. Am. Acad. Arts and Sci., 69 389 (1934).
9. Beattie, J.A., Bridgeman, O.C., J. Am. Chem. Soc. 50, 3133 (1928).
10. Benedict, M., Webb, G.B., Rubin, L.C., J. Chem. Phys. 8 334 (1940).
11. Benning, A.F., E.I. du Pont de Nemours, U.S. 2,641,579 (1953).
12. Benning, A.F., McHarness, R.C., Ind. Eng. Chem. 32, 497 (1940).
13. Benning, A.F., McHarness, R.C., Ind. Eng. Chem. 32, 698 (1940).
14. Benning, A.F., McHarness, R.C., Ind. Eng. Chem. 32, 814 980 (1940).
15. Bhada, R.K., "PVT Behavior of Carbon Tetrafluoride Using a Variable Volume Cell of Bellows Design", Ph.D. Thesis, The University of Michigan, Ann Arbor, Mich., 1968.
16. Bloomer, O.T., Inst. of Gas Technology Research Bulletin No. 13 May (1952).
17. Booth, H.S., Swinehart, C.F., J. Am. Chem. Soc. 57 1337 (1935).
18. Boys, S.F., Shavitt, I., Nature 178, 1340 (1956).
19. Boys, S.F., Shavitt, I., Proc. Roy. Soc. (London), A254, 487 (1960).
20. Boys, S.F., Shavitt, I., Proc. Roy. Soc. (London) A254 499 (1960).

21. Bridgman, P.W., Proc. Am. Acad. Arts and Sci. 49 1-114 (1913).

22. Bridgman, P.W., Proc. Am. Acad. Arts and Sci., 59 173 (1923).

23. Bridgman, P.W., Proc. Am. Acad. Arts and Sci., 66 185 (1931).

24. Bridgman, P.W., "The Physics of High Pressure", 2nd Ed., p. 126, G. Bell, London, England 1949.

25. Buckingham, R.A., Physical Chemistry in Aerodynamics and Space Flights, p. 205, Pergamon, New York (1961).

26. Buckingham, R.A., Corner, J., Proc. Roy Soc. (London) Ser. A, 189 118 (1947).

27. Burnett, E.S., J. Appl. Mech. 3 A136 (1936).

28. Cailletet, L., Ann. Chim. Phys. 19 386 (1880).

29. Canfield, F.B., The Compressibility Factor and Second Virial Coefficients for Helium-Nitrogen Mixtures at Low Temperatures and High Pressures", Ph.D. Thesis, Rice University, Houston, Texas (1962).

30. Canton, J., Phil. Trans. Roy. Soc., 640 (1762) ,261 (1964).

31. Carnazzi, Nuov. Cim. 5, 180 (1903).

32. Carrà, S., Konowalow, D.D., Nuovo Cimento 34, 205 (1964).

33. Chemical and Engineering News, 40, No. 2,49 (1962).

34. Cherney, B.J., Marchman, H., York, R., Ind. Eng. Chem. 41 2653 (1949).

34a. Chueh, P.L., Prausnitz, J.M., AIChE Journal 13, 1099 (1967).

34b. Chueh, P.L., Prausnitz, J.M., AIChE Journal 13, 1107 (1967).

35. Connolly, J.F., Kandalic, G.A., Phys. Fluids, 3, 463 (May-June 1960).

36. Connolly, J.F., Kandalic, G.A., Doc. No. 6307, Documentation Institute, Library of Congress, Washington, D.C.

37. Corner, J., Proc. Roy. Soc. (London) A192, 275 (1948).

38. Cutler, W.G., et al., J. Chem. Phys. 29 727 (Oct. 1958).

39. Doolittle, A.K., Simon, I., Cornish, M., A.I.Ch.E. Journal 6, 150 (March 1960).

40. Douslin, D.R., Moore, R.T., Dawson, J.P., Waddington, G., J. Am. Chem. Soc. 80, 2031 (May 1958).

41. Downing, R.C., E.I. du Pont de Nemours and Co., Wilmington, Del., Private Communication (1949).

42. Downing, R.C., E.I. du Pont de Nemours and Co., Wilmington, Del., Private Communications, X-57 B,C,D. (1965).

43. Downing, R.C., Modern Refrigeration, 777, (Sept. 1966).

44. Dymond,J.H., Rigby, M., Smith, E.B., J. Chem. Phys. 42 2801, (1965).

45. E.I. du Pont de Nemours, "Freon" Technical Bulletin RT-31.

46. E.I. du Pont de Nemours, and Co., Wilmington, Del., "Thermodynamic Properties of F-22", Freon Products Technical Bulletin (1964).

47. E.I. du Pont de Nemours, "Thermodynamic Properties of Freon-502 Refrigerant", Freon Technical Bulletin, T-502, 1963.

47a. Ekiner, O., Thodos, G., AIChE Journal 11, 847 (1965).

48. Ellington, R.T., Eakin, B.E., Chem. Eng. Prog. 59(11), 80 (1963).

49. Fender, B.E.F., Halsey, G.D., Jr., J. Chem. Phys. 36 1881 (1962).

50. Fitts, D.D., Ann. Rev. Phys. Chem. 17 59 (1966).

51. Fuoss, R.M., J. Am. Chem. Soc., 60 1633 (1936).

52. Giacomo, Arand di, Smyth, C.P., J. Am. Chem. Soc. 77 774 (1955).

52a. Grieves, R.B., Thodos, G., AIChE Journal 8 550 (1962).

53. Guggenheim, E.A., McGlashan, M.L., Mol. Phys. 3 563 (1960).

54. Guggenheim, E.A., McGlashan, M.L., Proc. Roy. Soc. (London), Ser. A, 255 456 (1960).

55. Hagenbach, W.P., Coming, E.W., Ind. Eng. Chem. 45 606 (1953).

56. Hill, T.L., Introduction to Statistical Thermodynamics, Addison-Wesley, Publishing Co., Reading, Mass. (1960).

57. Hilsenrath, J., et al., "Tables of Thermal Properties of Gases", U.S. Dept. of Commerce, National Bureau of Standards, Cir. 564, Washington, D.C.

58. Hirschfelder, J.O., Curtiss, C.F., Bird, R.B., Molecular Theory of Gases and Liquids, Wiley, New York, 1964.

59. Hirschfelder, J.O., McClure, F.T., Weeks, I.F., J. Chem. Phys. 10 201 (1942).

60. Horsley, L.H., "Azeotropic Data II", Advan. Chem. Ser. No. 35, 100 pp. (1965).

61. Hossain, S., Project ORA-01777, The University of Michigan, Ann Arbor, Michigan. (1967)

62. Hou, Yu-Chun, "Physical and Thermodynamic Properties of Trifluoromethane", Ph.D. Thesis, University of Michigan, Ann Arbor, Michigan, 1955.

63. Hougen, O.A., Watson, K.M., Ragatz, R.A., "Chemical Process Principles", Vol. II, John Wiley and Sons, New York, 1959.

64. Hudson, G.H., McCoubrey, J.C., Trans. Faraday Soc. 56, 761 (1960).

65. Isihara, A., J. Chem. Phys. 18 1446 (1950).

66. Isihara, A., Hayashida, T., J. Phys. Soc. Japan 6, 40 (1951).

67. Isihara, A., Hayashida, T., J. Phys. Soc. Japan 6, 46 (1951).

67a. Joffe, J., Ind. Eng. Chem. 39 837 (1947).

68. Kalfouglou, N.K., Miller, J.G., J. Phys. Chem. 71(5) 1256 (1967).

69. Kauzmann, W., Quantum Chemistry: An Introduction, Academic Press, New York, 1964.

70. Keesom, W.H., Comm. Phys. Lab. Leiden, Suppl. 24b, Section 6 (1912).

71. Keesom, W.H., Comm. Phys. Lab. Leiden, Suppl. 39a (1915).

72. Keller, J.B., Zumino, B., J. Chem. Phys. 30, 1351 (1959).

73. Keyes, F.G., Proc. Am. Acad. Arts and Sci. 68 505 (1933).

74. Kihara, T., Advan. Chem. Phys. 5 147 (1963).

75. Kihara, T., J. Phys. Soc. Japan 6 289 (1951).

76. Kihara, T., Rev. Mod. Phys. 25 831 (1953).

77. Kihara, T., Supplement of the Progress of Theoretical Physics 40 177 (1967).

78. Kihara, T., Koba, S., J. Phys. Soc. Japan 9, 688 (1954).

79. Klein, M., U.S. Clearinghouse, Fed. Sci. Tech. Inform. AD649463, 98 pp. (1967).

80. Klezkii, A.W., Inzh-Fiz. Zh. Akad. Nauk. Belorussk. SSR 7(4) 40 (1964).

81. Konowalow, D.D., Guberman, S.L., Ind. Eng. Chem. Fundam., 7(4) 622 (1968).

82. Konowalow, D.D., Taylor, M.H., Hirschfelder, J.O., Phys. Fluids 4 622 (1961).

82a. Kreglewski, A., Kay, W.B., J. Phys. Chem. 73 3359 (1969).

83. Lagutina, L.M., Cholodil'naja technika 43 25 (1966).

84. Lange, N.A., "Handbook of Chemistry", Handbook Publishers, Inc., Sandusky, Ohio,1961.

84a. Leland, T.W. Jr., Mueller, W.H., Ind. Eng. Chem. 51 597 (1959).

85. Lennard-Jones, J.E., Proc. Roy. Soc. (London) A106 463 (1924).

85a. Li, C.C., Can. Journal Chem. Eng. 19, 709 (1971).

85b. Li, C.C., Chen, T.Y., Murphy, K.P., Paper presented at the Las Vegas AIChE Meeting, September 1964.

86. Löffler, H.J., Kaeltetechnik 19(7), 201 (1967).

87. Löffler, H.J., Matthias, H., Käeltetechnik 18(11) 408 (1966).

88. Long, L.J., Master's Thesis, University of Delaware (1961).

89. Martin, J.J., Ind. Eng. Chem. 59, No. 12, 34 (1967).

90. Martin, J.J., Downing, R.C., "Thermodynamic Properties of Refrigerant 502", ASHRAE Annual Meeting, Kansas City, Missouri, June 28-July 1, 1970.

91. Martin, J.J., Hou, Y.C., AIChE J. 1 142 (1955).

92. Martin, J.J., Hou, Y.C., AIChE J. 5 125 (1959).

93. Martin, J.H., Kapoor, R.M., Shinn, R.D., Proc. II. Congr. Eur. Fed. Chem. Eng., Frankfurt, Germany, Dechema-Manographien, 32 48 (1958).

94. Mason, E.A., J. Chem. Phys. 23 49 (1955).

95. Mason, E.A., Spurling, T.H., "The Virial Equation of State", The International Encyclopedia of Physical Chemistry and Chemical Physics, Pergamon Press, New York 1969.

96. McHarness, R.C., Chapman, D.D., ASHRAE Jour. 4, No. 1, 49 (1962).

97. McWilliams, T.G., "Homoazeotropy in Some Refrigerant Systems", Univ. Microfilms, Ann Arbor, Mich., Order No. 65-617, 140 pp.

98. Mears, W.H., Rosenthal, E., Sinka, J.V., J. Chem. Eng. Data 11(3) 338 (1966).

99. Michels, A., Private Communication (1957).

100. Michels, A., Gibson, R.O., Ann. Physik., 87 850 (1928).

101. Michels, A., Michels, C., Proc. Roy. Soc. (London), 153(A) 201 (1935).

102. Midgley, T. Jr., Henne, A.L., Ind. Eng. Chem. 22 542 (1930).

103. Mie, G., Ann. Physik., 11 657 (1903).

104. Morse, P.M., Phys. Rev. 34 57 (1929).

105. Mueller, W.H., Leland, T.W. Jr., Kobayashi, R., AIChE J. 7 267 (June 1961).

106. Munn, R.J., J. Chem. Phys. 40 1439 (1964).

107. Nain, V.P.S., Saksena, M.P., Chem. Phys. Lett. 1(4) 125 (1967).

108. Nain, V.P.S., Saxena, S.C., Indian J. Phys. 41(3) 199 (1967).

109. O'Connell, J.P., Prausnitz, J.M., "Advances in Thermophysical Properties at Extreme Temperatures and Pressures", Symp. Thermophysical Properties, Lafayette, Ind. 19-31 (1965).

110. Parsons, C.A., Cook, S.S., Proc. Roy. Soc. 85 332 (1911).

111. Pennington, W.A., Air Conditioning, Heating and Ventilating, 55(11) 71 (1958).

112. Pennington, W.A., World Refrig. 8 85, 151 (1957).

113. Perkins, J., Trans. Roy. Soc. 72 324 (1819-20).

114. Perry, J.H., editor, "Chemical Engineers Handbook", McGraw-Hill, New York, 3rd Ed., 1963.

115. Pfefferle, W.C. Jr., Goff, J.A., Miller, J.G., Chem. Phys. 23 509 (1955).

116. Power, E.A., Advanc. Chem. Phys. 12 167-224 (1967).

117. Prausnitz, J.M., Molecular Thermodynamics of Fluid-Phase Equilibria, Prentice-Hall, Inc., Englewood Cliffs, New Jersey 1969.

118. Prausnitz, J.M., Keeler, R.N., AIChE J. 7, 399 (1961).

119. Prausnitz, J.M., Myers, A.L., AIChE J. 9 5 (1963).

120. Reid, R.C., Sherwood, T.K., "The Properties of Gases and Liquids", McGraw-Hill, Inc., New York, 2nd Ed. (1966).

121. Richards, T.W., Pub. Carnegie Inst. Washington, No. 7, (1903).

122. Rowlinson, J.S., J. Chem. Phys. 19 827 (1951).

123. Rowlinson, J.S., Trans. Faraday Soc. 45 974 (1949).

124. Saxena, S.C., Gambhir, R.S., Mol. Phys. 6 577 (1963).

125. Schamp, H.W., Mason, E.A., Richardson, A.C.B., Altman, A., Phys. Fluids 1, 329 (Aug. 1958).

126. Schneider, W.G., Canadian J. of Research 27B, 339 (1949).

127. Silberberg, I.H., Kobe, K.A., McKetta, J.J., J. Chem. Eng. Data 4 314 (Oct. 1959).

128. Singer, K., Nature 181 262 (1958).

129. Smyth, C.P., McAlpine, K.B., J. Chem. Phys. 1 190 (1933).

129a. Sonntag, R.E., Van Wylen, G.J., "Fundamentals of Statistical Thermodynamics", Wiley, New York 1966.

130. Soumerai, H., ASHRAE Jour. 6, No. 1, 31 83 (1964).

130a. Spencer, C.F., Daubert, T.E., Danner, R.P., "A Critical Review of Correlations for the Critical Properties of Defined Mixtures", Paper presented at the 65th Meeting of AIChE at New York, Nov. 27-Dec. 2, 1972.

131. Stein, W.A., "Methoden zum. Aufstellen von Zustandsgleichungen fur reine fluide Stoffe", Diss. T.H. Braunschweig, 1965.

132. Stockmayer, W.H., J. Chem. Phys. 9 398 (1941).

133. Storwick, T.S., Spurling, T.H., J. Phys. Chem. 72(5) 1821 (1968).

134. Suh, K.W., Storvick, T.S., J. Phys. Chem. 71(5) 1450 (1967).

135. Tait, P.G., Report of the Voyage of H.M.S. "Challenger II", Appendix A (1881).

136. University of Michigan, Engineering Research Institute, "Thermodynamic Properties of F-115", Project M777, 1951.

137. Varshni, Y.P., Revs. Modern Phys. 29 664 (1957).

138. Vora, B.P., Project ORA 01777, The University of Michigan, Ann Arbor, Michigan, (1967)

139. Woolrich, W.R., "Handbook of Refrigerating Engineering", Vol. 1, The AVI Publishing Company, Inc., Westport, Conn (1965).

140. Zander, M., Proc. Symp. Thermophys. Prop. 4th., 114 (1968).