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A GENERALIZED EQUATION OF STATE FOR MIXTURES

by

Aksel Öztürk

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
(Mechanical Engineering)
in The University of Michigan
1972

Doctoral Committee:

Professor Richard E. Sonntag, Chairman
Professor Vedat S. Arpacı
Professor Joseph J. Martin
Associate Professor Gene E. Smith

To my mother, Zarife Öztürk

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NOMENCLATURE

Symbols

A	area
A	Martin function defined by (3-26a)
A	modified Martin constant
A	modified Martin function defined by (4-25a)
A_o	Benedict-Webb-Rubin constant
a	Benedict-Webb-Rubin constant
a	Martin constant
B	Martin function defined by (3-26b)
B	modified Martin constant
B	modified Martin function defined by (4-25b)
B	second virial coefficient
B'	second virial coefficient
B_o	Benedict-Webb-Rubin constant
b	Benedict-Webb-Rubin constant
b	Martin constant
C	correction parameters for pressure calculation
C	Martin function defined by (3-26c)
C	modified Martin constant
C	modified Martin function defined by (4-25c)
C	parameter for the curvature of isometrics defined by (4-28)
C	third virial coefficient
C'	parameter for the slope of isometrics defined by (4-31)
C'	third virial coefficient

NOMENCLATURE (Con'd)

Symbols

C_o	Benedict-Webb-Rubin constant
C_v	constant volume specific heat
c	Benedict-Webb-Rubin constant
c	Martin constant
D	diameter
D	fourth virial coefficient
Dev. %	percentage deviation defined by (4-14)
d	Martin constant
f	any explicit function
f	correction factor for pressure
f	hydrostatic pressure correction defined by (6-13)
f	Martin function defined by (3-23a) and (3-24a)
G	modified Martin function defined by (3-31)
g	Martin function defined by (3-25b)
g_C	conversion factor in English Engineering system
g_L	local gravitational acceleration
g_S	standard gravitational acceleration
HRP	high range piston for pressure gages
h	height for hydrostatic pressure
K	dummy constant for writing general combining rule
k	Martin constant
k	modified Martin constant
L	length
LRP	low range piston for pressure gage

Symbols

M	molecular weight
m	ratio of α_{r7} to α_{r6}
m	slope of isometrics
N	number of components in mixtures
n	number of moles
P	pressure
R	random error
R	universal gas constant
S	systematic error
S	Strobridge constant
S	modified Strobridge constant
T	temperature
TM	total mass on pressure gages
TW	total weight on pressure gages
t	Martin constant
V	total volume
v	specific volume
x	constants defined by (4-10a,b)
y	constants defined by (4-10a,b)
y	mole fraction
Z	compressibility factor

Greek Symbols

α	Benedict-Webb-Rubin constant
α	constants in mass determination defined by (5-9) and (5-10)

NOMENCLATURE (Con'd)

Greek Symbols

α	Martin constant
α	modified Martin constant
α	thermal strain
α_c	Riedel factor
β	reduced second virial coefficient
γ	Benedict-Webb-Rubin constant
γ	reduced third virial coefficient
γ_v	thermal-pressure coefficient
Δ	difference
Δ	matrices
Δ	uncertainty
δ	constant in mass determination defined by (5-11)
δ	reduced fourth virial coefficient
ε	reduced derivatives of the critical isotherm at the critical point
Θ	modified Martin function defined by (3-33a)
θ	virial coefficient function
λ	constants defined by (4-24)
μ	constants defined by (4-24)
ρ	molal density
τ	modified Martin constant on critical isotherm
τ	modified Martin function defined by (3-34a)
ϕ	explicit function
ϕ	modified Martin function defined by (3-34b)
φ	modified Martin function defined by (3-33b)
ω	acentric factor

Subscripts

1	initial equilibrium state in volume measurement
1	property calculated with the critical constant
1	property after first expansion in the mass determination
1,....,7	Martin subscripts
1,....,7	modified Martin subscripts
1,....,16	Strobridge subscripts
1,....,18	modified Strobridge subscripts
2	final equilibrium state in volume measurement
2	property after second expansion in the mass determination
2	second virial coefficient
3	third derivative of critical isotherm
3	third virial coefficient
4	fourth derivative of critical isotherm
4	fourth virial coefficient
I	expansion tank I
II	expansion tank II
APG	air piston gage
atm	atmospheric
B	Boyle temperature
BAR	barometric
C	property for the test cell
c	critical property
cal	calculated property
cm	pseudo-critical property

Subscripts

DPI	differential pressure indicator
DWG	dead weight gage
exp	experimental property
g	gage
H	header
i,ii,iii	pure component i
i	segments in mass determination
ij	interaction between pure components i and j
ijk	interaction between pure components i, j, and k
L	corresponding constants for the combining rule
M	filled with mercury for volume measurement
m	mixture
nom	nominal value
r	reduced property
ref	reference
sat	saturated property
T	property for the tank
U	unknown value
x	particular property
y	particular property
z	particular property

Superscripts

o	simple fluids
1	deviation from simple fluids
'	particular temperature defined on p. 77
"	particular temperature defined on p. 77

CHAPTER I

INTRODUCTION

In Science and Engineering, it is very desirable to be able to predict the PvT behavior of mixtures by means of an equation of state having the same form as that for the pure substances and whose constants may be determined from related constants of the equation of pure constituent components. This analytical PvT relation is also needed to calculate the thermodynamic properties-such as enthalpy, entropy, heat capacity, and fugacity-of mixtures. Many equations of state for pure substances have been proposed since van der Walls (1873); however, very few of these have been tested for mixtures. Those equations which have been applied to mixtures are not very satisfactory for the critical region and for higher densities.

The eight-constant Benedict-Webb-Rubin (BWR) equation (1940), one of the most frequently used and developed equations for mixtures, has been tested primarily for light hydrocarbons and for only a few non-hydrocarbons. Other equations, like the two-constant Redlich-Kwong (RK) and the five-constant Beattie-Bridgeman (BB) equations, are less accurate, especially near the critical region and higher densities.

The more accurate twelve-constant Martin-Hou (MH) equation (1959) has been successful in estimating carbon dioxide-nitrogen mixtures (1963) and, although mixture rules have been suggested it has not yet been tested with other mixtures.

In recent years, because of the availability of high-speed computers, many new attempts have been made to obtain better agreement between experimental and calculated PvT behavior by means of multi-constant equations, but these have not been thoroughly tested. Almost no other

equation more accurate than the BWR equation has been thoroughly developed and tested with mixtures.

It is desirable to develop a high precision equation of state for mixtures in order to be able to predict the thermodynamic properties and phase behavior of various mixtures with a high degree of accuracy. Therefore, in this research an attempt was made to develop a generalized 21-constant equation of state for mixtures that is similar in form to Martin's recent equation. This equation was applied first to the pure components, namely, argon, neon, and nitrogen, for which constants were not available. The constants were determined by the method of successive approach, then the equation was tested primarily with argon-nitrogen data available in the temperature range 143.15 K to 273.15 K using a new combining rule obtained from corresponding states theory.

Also, some new experimental PvT data for argon-neon and neon-nitrogen mixtures in the temperature range 90 K to 140 K were measured by the final expansion method; the results were then used to test the equation.

CHAPTER II

LITERATURE SURVEY

A. EQUATION OF STATE

1. General. Equations of state have been developed by three different approaches: theoretical, empirical, and generalized. In the theoretical approach, the equation of state is obtained by means of the partition function of statistical thermodynamics or the virial theorem of statistical mechanics. The equation can then be transformed into the virial form which expresses the compressibility factor as a power series in density. The virial coefficients (which are contributions from two-particle interactions, three-particle interactions, etc.) are functions only of temperature. There is considerable information available on the virial equation of state up to the third virial coefficient (6, 15, 44, 69).

However, some equations - including the four-constant Keyes equation (47), the five-constant Beattie-Bridgeman (BB) equation (5), and the eight-constant Benedict-Webb-Rubin (BWR) equation (11) - were developed empirically using least-squares or other mathematical procedures in order to obtain the constants and then were tested for a number of substances. As the number of constants increases the applicable density range is increased with high precision. For example, though the BB equation gives results of intermediate accuracy, the BWR equation much more accurately represents the PvT behavior of substances to about twice critical density (3).

The BWR equation initially was developed (1940) for light hydrocarbons (7, 11), then it was applied and tested to other substances for PvT behavior and vapor-liquid equilibria (25,27,46,65,73,81,83,93,106).

An excellent collection of the available BWR constants has been presented by Cooper and Goldfrank (22). Recently (1970), a new set of constants for the BWR equation - primarily for hydrocarbons, including neon - was published (68). Yendall has applied a modified BWR equation with 12 constants to neon (104). Strobridge used a new equation for nitrogen with 16 constants developed from the BWR equation (96). It is currently considered to be the best equation of state for nitrogen. McCarty and Stewart (1964) listed the constants of the Strobridge equation for neon (51). Crain and Sonntag (1965) determined the constants for argon and nitrogen from the new experimental PvT data in the temperature range 143.15 K to 273.15 K (24). Recently (1969), Gosman, McCarty and Hust redetermined the constants for argon (35). At the same time McCarty and Stewart modified the Strobridge equation with 18 constants for neon (52,53). Then (1968) Gibbons and Kuebler redetermined the 18 constants on the basis of new PvT data (34).

In the third type of approach - that of generalized equations such as Redlich-Kwong (RK) (74) and Martin-Hou (MH) (59, 60) - the constants are evaluated from the general behavior of substances. The RK equation is known as the best two parameter equation; however, it often gives poor results. Therefore, numerous modifications of the RK equation have appeared in recent years. Gray et al recently (1970) presented a summary of previous work which attempted to improve the RK equation (36).

Besides generalized equations, some investigators have generalized empirical equations in reduced forms. Su and Viswanath (1965) determined the generalized constants of the BWR equation for both hydrocarbons and non-hydrocarbons using generalized compressibility charts

based on experimental data (97). Cooper and Goldfrank (1967) listed two different sets of generalized constants for hydrocarbons and non-hydrocarbons (22).

2. Equation of State for Mixtures. The eight-constant BWR equation is the best known equation of state for mixtures. Prior to this equation, the other, few equations such as the four-constant Keyes equation and the five-constant BB equation were developed for mixtures (12). In many books (4,30,76) and papers (3,12) there is adequate information and references about those early works.

The BWR equation, which was first applied and tested for light hydrocarbons (7,8,12) gives satisfactory representation of the PvT behavior of mixtures with the given combination rules in order to obtain mixture constants from the pure component constants. Then this equation was widely used to correlate vapor-liquid equilibrium for different mixtures and was discussed in many papers (9,10,27,65,72,81,93). Crain and Sonntag tested the equation for the PvT behavior of argon-nitrogen system (25).

Recently (1970), Starling and Powers developed an eleven-constant modified BWR equation in order to predict enthalpy behavior of mixtures and tested it with the methane-propane system (90).

Crain and Sonntag (1965) (24), tried to apply the more accurate Strobridge equation to argon-nitrogen system and others (87) have tried to apply the same equation to different binary systems; it has been found to be impossible to find any reasonable correspondence between related constants as a function of composition.

Because of its simplicity, the two-constant RK equation (74) has been used extensively for mixtures since it was developed in 1949.

Improvements to the RK equation for mixtures were presented in some recent papers (36,99). Recently (1970, 1971), Sugie and Lu attempted to develop a modified RK equation for mixtures by shifting the horizontal inflection point to the critical point (the same modification had been done previously (1967) to the van der Waals equation by Martin (57)), and they also added a new deviation which is power series in density (98, 99). They tested it successfully for PvT behavior and enthalpy departure with a few mixtures.

Ackerman compared the RK and the BWR equation for 26 binary mixtures at the critical region. The presented results do not reveal a clear advantage of either the BWR or the RK equation in the critical region (1).

Smith, Sonntag, and Van Wylen (1963) suggested a combining rule for the MH equation and tested it only for carbon dioxide-nitrogen system (85).

3. Martin's Equation of State. Martin and Hou (1955) developed a new equation of state whose constants might be determined from the general behavior of substances (59). Later (1959), a modified MH equation was proposed with 12 constants instead of 10 (60). The constants of the original equation were calculated for seven different gases and the equation was tested, with a very high degree of accuracy, up to about 1.5 times critical density. The modified equation was applied to carbon-dioxide (60) with even greater precision. Then, Smith, Sonntag, and Van Wylen (1963) investigated the accuracies of several combining rules for the modified MH equation for mixtures and then tested it for the carbon dioxide-nitrogen system (85,86). Since then, no application of this equation for mixtures has been found. In 1962 Martin proposed a

slightly different equation (58). Martin then (1967) improved the equation of state for high densities by using new exponential terms (57). This equation was tested with 16 constants for chlorodifluoromethane and was applied to carbon dioxide only for the critical isotherm with better precision.

B. PvT DATA

1. Pure Substances.

ARGON DATA: The PvT behavior of argon has been adequately studied experimentally and numerous papers have been published over many years. The data which is available in the literature has been referenced in detail in many works (2,21,23,28,40,66,67). Crain, Sonntag, and Van Wylen (1965) researched previous PvT data of argon and collected some experimental data for the isotherms 143.15, 163.15, 203.15, and 273.15 K in the pressure range up to about 500 atm (26). In addition to that data are the data collected by Michels, Levelt, and DeGraff (63) in the temperature range 120.65 K to 248.15 K at pressures up to 850 atm, by Rogovaya and Kaganer (79) in the temperature range 138.15 to 248.17 K at pressures up to about 200 atm, and by Michels, Wijker, and Wijker (64) at temperatures from 273.15 K to 423.15 K, at pressures up to 1800 atm. All of the preceding data (Table I) were used in this work in order to test the equation of state.

TABLE I

NUMBER OF EXPERIMENTAL PvT DATA POINTS OF ARGON, NEON, AND NITROGEN

TESTED FOR THE EQUATION OF STATE

	No. of Data Points	Pressure Range (atm)	Spec. Volume Range (cc/mole)	Temperature Range (K)
1. ARGON:				
11) Crain-Sonntag (24)	77	2 - 510	39 - 10000	143 - 273
12) Michels-Levelt-DeGraaff (63)	270	6 - 850	39 - 2700	118 - 248
13) Michels-Wijker-Wijker (64)	63	18 -1800	38 - 1200	273 - 423
14) Rogovaya-Kaganer (79)	53	27 - 200	40 - 720	163 - 248
2. NEON:				
21) Scott-Sonntag (82)	125	1 - 230	20 - 6600	38 - 70
22 23 Gibbons (33)	224	4 - 200	19 - 670	34 - 70
24) Sullivan-Sonntag (100)	81	7 - 300	24 - 970	70 - 120
3. NITROGEN:				
31) Sonntag-Öztürk (88)	26	20 - 190	45 - 70	110 - 140
32) Friedman (31)	75	1 - 200	65 - 14000	100 - 300
33) Crain-Sonntag (24)	90	2 - 510	43 - 10000	143 - 273
34) Canfield-Leland-Kobayashi (18)	150	2 - 540	41 - 8900	133 - 273
35) Weber (103)	40	25 - 110	53 - 105	120 - 140
36) Streett-Stavely (95)	9	17 - 100	44 - 51	110 - 120

TABLE II

CRITICAL CONSTANTS OF ARGON, NEON AND NITROGEN

Substance	M	T_c,K	$P_c$atm.	v_c,cc/mole
Argon	39.944	150.86 (63)	48.34 (63)	74.56 (63)
Neon	20.183	44.4 (37)	26.19 (37)	41.744(61)
Nitrogen	28.016	126.2 (48)	33.5 (48)	90.1 (48)

The critical constants for argon were listed by Michels, Levelt, and DeGraaff (1958) (63). Although different values of the critical constants have been published (41,48), those which were used in this work were considered to be the best values available (Table II).

No experimental PvT data for the critical isotherm (150.86 K) were found in the literature, but 20 data points were obtained by linear interpolation between isotherms 150.65 and 153.15 K from Michels', et al data (63) (Table III-1).

NEON DATA: Sullivan and Sonntag (1966) (101) and Scott and Sonntag (1967) (82) searched the literature for the available experimental PvT data of neon. Other reports and texts (2,21,66,67,100) also list numerous references for neon data. Sullivan and Sonntag published (1966) 81 data points at four isotherms from 70 to 120 K, pressures up to 300 atm (100,101) and then Scott and Sonntag measured, in 1967, 142 data points at temperatures 30 to 70 K, pressures up to 200 atm (82). Recently (1968), Gibbons obtained new data in the range from 27 to 70 K at pressures up to 200 atm (33). All those data were used to obtain the constants of the equation of state for neon (Table I).

TABLE III-1

CRITICAL ISOTHERM DATA OF ARGON

DATA NO (*)	P ATM.	V CC/MOLE
2015	302.684	34.916
2025	211.954	35.815
2035	150.897	38.835
2045	110.288	41.005
2055	86.328	43.099
2065	65.533	46.420
2075	57.203	49.108
2085	52.757	51.822
2095	50.203	55.002
2105	48.558	62.167
5	48.340	74.560
2115	47.564	107.641
2125	46.359	126.970
2135	44.123	150.924
2145	40.142	189.509
2155	35.695	235.640
2165	30.769	297.371
2175	25.451	386.535
2185	21.432	480.811
2195	16.414	660.902
2205	11.397	995.756
2215	7.396	1585.804

(*) 2000 MICHELS-LEVELT-DEGRAAFF DATA (63)

TABLE III-2

CRITICAL ISOTHERM DATA OF NEON

DATA NO (*)	P ATM.	V CC/MOLE
2015	180.119	19.256
1015	129.199	20.261
2025	98.227	21.050
1025	72.420	22.152
2035	46.853	24.046
1035	41.739	24.837
2045	31.611	27.178
1045	29.508	28.303
1055	27.305	30.851
2055	26.697	32.451
2065	26.584	33.786
1065	26.468	35.811
1075	26.308	38.640
2075	26.305	39.144
1085	26.202	40.079
5	26.190	41.744
2085	25.371	66.865
2095	23.957	82.637
1095	23.647	85.894
2105	21.750	104.274
1105	21.324	107.924
1115	16.651	163.338
2115	12.736	233.609
1125	12.602	236.595
2125	8.787	364.935
2135	5.809	579.950

(*) 1000 SCOTT-SONNTAG DATA (82)
2000 GIBBONS DATA (33)

The critical temperature and pressure for neon, which were measured by Grilly (37), and the critical density measured by Mathias et al (61), were selected as more accurate values than the others. Also, McCarty, Stewart, and Timmerhaus (54) and Scott and Sonntag (82) were in agreement with those values (Table II).

PvT data for the critical isotherm, 44.4 K, was found in Scott and Sonntag's data and in Gibbon's data and some points were obtained by linear interpolation from the same data (Table III-2).

NITROGEN DATA: A quantity of experimental PvT data for nitrogen can be found in the literature; most of this reported data, however, is fragmentary and incomprehensive. Recently, more comprehensive data, in various ranges, has been reported. The bibliography for the earlier experimental PvT data of nitrogen can be located in several texts, reports, and papers (21,26,29,66,67). Some of the recently collected data were used in this work for testing the equation of state. Crain and Sonntag reported data for four isotherms (143.15, 163.15, 203.15, and 273.15 K) at pressures up to 500 atm (24). Streett and Stavely measured data, in 1967, for the compressed liquid region, in the temperature range 77.35 to 120.23 K, at pressures up to 680 atm (95). In 1969 Sonntag and Öztürk collected PvT data for the critical region in the temperature range 110 to 140 K for five isochors from 45 cc/mole to 70 cc/mole (88) (Table IV). Later (1970), Weber published data in the temperature range 80 to 140 K and at densities 0.85 to 2.6 times critical density (103). In addition to those data, Canfield's (18) and Friedman's (31) data were used in this study for the other isotherms and low densities (Table I).

The critical constants of nitrogen were chosen from Kobe and Lynn (48) as the most accurate values (Table II).

Some of the PvT data for the critical isotherms were found in Friedman's data (31) and the remainder were obtained from Sonntag and Öztürk data measured in the thermodynamic laboratory (Table III-3).

2. Mixtures

In the past, extensive studies on thermodynamic properties of mixtures have been initiated and large numbers of papers about experimental work for mixtures - including PvT data for various mixtures - have appeared in the literature. Crain, Sonntag, and Van Wylen (26) in 1965- besides collecting PvT data for three different compositions of the argon-nitrogen system at the temperatures 143.15, 163.15, 203.15, and 273.15 K and pressures up to 520 atm - also researched and presented several comprehensive references for mixtures of different substances. In addition to that work, Clark, Hyman and Wilson (21), in 1966, reported the available data for the thermophysical properties of cryogenic binary mixtures.

Because of the scope of this present work, only the literature for the PvT data of mixtures - either binary or ternary - of argon, neon, and nitrogen were surveyed. Zandbergen and Beenakker (105), in 1967, measured PvT behavior for three different systems - including argon-nitrogen - at several concentrations between 170 and 292 K and at pressures 3 and 100 atm in order to determine the volume change of the mixing process. Besides this, no experimental PvT data were found for either neon-nitrogen or argon-neon systems.

TABLE III-3

CRITICAL ISOTHERM DATA OF NITROGEN

DATA NO (*)	P ATM.	V CC/MOLE
1215	130.335	44.971
1315	71.540	49.701
1225	47.127	54.895
1325	36.241	62.348
2015	34.530	65.992
2025	33.900	69.782
1335	33.963	69.975
1115	33.581	77.695
2035	33.510	81.142
5	33.500	90.100
2045	33.460	107.853
2055	33.170	127.244
2065	33.080	130.504
2075	32.390	148.984
2085	31.870	159.034
2095	31.340	169.325
2105	30.160	190.155
2115	29.110	207.776
2125	27.280	238.717
2135	23.130	317.418
2145	19.160	417.721
2155	11.930	754.421
2165	8.110	1165.912
2175	6.513	1480.341

(*) 1000 SONNTAG-OZTURK DATA (88)
2000 FRIEDMAN DATA (31)

TABLE IV

EXPERIMENTAL PvT DATA OF NITROGEN

IN THE CRITICAL REGION

(88)

Data No.	T K	P atm	v cc/mole	Z
1211	110.269	20.036	44.758	0.099
1212	114.073	46.428	44.822	0.222
1213	118.022	73.885	44.872	0.342
1214	122.004	101.461	44.920	0.455
1215	126.198	130.319	44.971	0.566
1216	130.010	156.380	45.017	0.660
1217	135.037	190.442	45.072	0.775
1313	117.997	28.739	49.586	0.147
1314	122.002	49.577	49.645	0.246
1315	126.202	71.552	49.702	0.343
1316	130.003	91.499	49.746	0.427
1317	135.022	117.925	49.801	0.530
1318	140.014	143.988	49.861	0.625
1223	118.008 sat	22.415	54.786	0.127
1224	121.998	30.342	54.842	0.166
1225	126.206	47.152	54.895	0.250
1226	130.004	62.644	54.942	0.323
1227	134.999	83.195	55.014	0.413
1228	140.027	103.931	55.065	0.498
1325	126.199	36.240	62.347	0.218
1326	130.003	47.564	62.398	0.278
1327	135.004	62.834	62.469	0.354
1328	139.996	78.309	62.533	0.426
1335	126.201	33.965	69.976	0.230
1336	129.993	42.807	70.035	0.281
1337	135.011	54.943	70.099	0.348
1338	139.995	67.258	70.160	0.411

CHAPTER III

THEORETICAL DERIVATIVES AND GENERAL BEHAVIOR OF SUBSTANCES

A. EQUATIONS OF STATE

1. General. An equation of state for gas mixtures is expressed as an analytical relation of pressure, volume, temperature and mole numbers of the pure components in the mixture:

$$f(P,v,T,n_i) = 0, \quad i = 1,2,\ldots,N \tag{3-1}$$

where N is the number of pure components. Generally, it is desirable to express one of the properties, e.g. pressure, in terms of the others:

$$P = P(v,T,n_i), \quad i = 1,2,\ldots,N \tag{3-2}$$

It is generally considered that the equation of state for mixtures should have the same form as that of the pure substances and that each constant for the mixture, say K_{mL}, would be the function of corresponding parameters of pure components and mole numbers:

$$K_{mL} = K_{mL}(K_{iL},n_i), \quad i = 1,2,\ldots,N \tag{3-3}$$

where K_{iL}'s are the corresponding constants of the pure components. Therefore, it is necessary to know or to determine the pure component constants. Then, it is necessary to know a set of combining rules, relations of the equation (3-3), in order to find the mixture constants.

2. Combining Rules. Several form of the combining rules have been proposed to determine the mixture constants. The procedure for obtainining combining rules, usually, starts from the theoretical rule given for the second, third, etc. virial coefficients of mixtures by Mayer (62), such as,

$$K_m = \sum_i^N \sum_j^N y_i y_j K_{ij} \tag{3-4}$$

or

$$K_m = \sum_i^N \sum_j^N \sum_k^N y_i y_j y_k K_{ijk} \tag{3-5}$$

etc. Here $y_i = n_i / \sum_i^N n_i$ is the mole fraction of component i in the mixture. K_{ij} is the parameter characterizing the interaction between component i and component j. Early scientists proposed several relations as follows:

Linear combination (13) $$K_{ij} = \frac{1}{2}(K_i + K_j) \tag{3-6}$$

Square-root combination (32) $$K_{ij} = (K_i K_j)^{1/2} \tag{3-7}$$

Lorentz combination (50) $$K_{ij} = \left(\frac{K_i^{1/3} + K_j^{1/3}}{2}\right)^3 \tag{3-8}$$

K_{ijk} is the constant characterizing the interaction between components i,j, and k.

Smith (84) discussed third order combinations such as:

Linear combination $$K_{ijk} = \frac{1}{3}(K_i + K_j + K_k) \tag{3-9}$$

Cubic-root combination $$K_{ijk} = (K_i K_j K_k)^{1/3} \tag{3-10}$$

Linear cubic-root combination (Lorentz combination) $$K_{ijk} = \left(\frac{K_i^{1/3} + K_j^{1/3} + K_k^{1/3}}{3}\right)^3 \tag{3-11}$$

Substituting linear combinations, equations (3-6) and (3-9), into equations (3-4) and (3-5), respectively,

$$K_m = \sum_i^N y_i K_i \tag{3-12}$$

is obtained in the same manner, the linear combining rule. By square-root combination, equation (3-7), and cubic-root combination, equation (3-10),

$$K_m = \left(\sum_i^N y_i K_i^{1/2}\right)^2 \tag{3-13}$$

$$K_m = \left(\sum_i^N y_i K_i^{1/3}\right)^3 \tag{3-14}$$

linear square-root and linear cubic-root combining rules are obtained from equations (3-4) and (3-5) respectively. This may be generalized as a linear L^{th} root combining rule for the coefficients of L^{th} power of the density by,

$$K_m = \left(\sum_i^N y_i K_i^{1/L}\right)^L \tag{3-15}$$

With the others, equations (3-8) and (3-11), Lorentz combining rules may be derived such as

$$K_m = \sum_i^N \sum_j^N y_i y_j \left(\frac{K_i^{1/3} + K_j^{1/3}}{2}\right)^3 \tag{3-16}$$

and

$$K_m = \sum_i^N \sum_j^N \sum_k^N y_i y_j y_k \left(\frac{K_i^{1/3} + K_j^{1/3} + K_j^{1/3}}{3}\right)^3 \tag{3-17}$$

3. Benedict-Webb-Rubin Equation (BWR). The BWR equation of state (11) is represented by

$$P = \frac{RT}{v} + \frac{RTB_o - A_o - C_o/T^2}{v^2} + \frac{RTb - a}{v^3} + \frac{a\alpha}{v^6} + \frac{c/T^2}{v^3}\left(1 + \frac{\gamma}{v^2}\right)e^{-\frac{\gamma}{v^2}} \tag{3-18}$$

which contains eight adjustable constants. This equation gives an accurate representation of PvT behavior to about twice the critical density.

Cooper and Goldfrank (22) summarized this equation and listed the constants for 38 substances. They also correlated the reduced constants of the reduced BWR equation as follows,

$$P_r = \frac{T_r}{v_r'} + \frac{B_{o_r}T_r - A_{o_r} - C_{o_r}/T_r^2}{v_r'^2} + \frac{b_r T_r - a_r}{v_r'^3} + \frac{a_r \alpha_r}{v_r'^6} + \frac{c_r/T_r^2}{v_r'^3}\left(1 + \frac{\gamma_r}{v_r'^2}\right)e^{-\frac{\gamma_r}{v_r'^2}} \qquad (3\text{-}19)$$

where $v_r' = \frac{v}{RT_c/P_c} = Z_c \frac{v}{v_c}$ and

$$B_{o_r} = B_o P_c/RT_c = 0.129426$$

$$A_{o_r} = A_o P_c/R^2T_c^2 = 0.284623$$

$$C_{o_r} = C_o P_c/R^2T_c^4 = 0.157489$$

$$b_r = bP_c^2/R^2T_c^2 = 0.027364 \qquad (3\text{-}20)$$

$$a_r = aP_c^2/R^3T_c^3 = 0.020839$$

$$\alpha_r = \alpha P_c^3/R^3T_c^3 = 0.0019427$$

$$c_r = cP_c^2/R^3T_c^5 = 0.023222$$

and

$$\gamma_r = \gamma P_c^2/R^2T_c^2 = 0.052603$$

for non-hydrocarbons, (22)

A number of different investigators (12,25,27,72,93) have successfully applied the equation to mixtures with the combining rules given in Table V.

TABLE V

THE COMBINING RULES OF THE BWR EQUATION OF STATE

Constants	Combining Rule
B_o	$K_m = \sum\sum y_i y_j \left(\frac{K_i^{1/3}+K_j^{1/3}}{2}\right)^3$
A_o, C_o, $\mathcal{T}$	$K_m = \left(\sum y_i K_i^{1/2}\right)^2$
a, b, c, α	$K_m = \left(\sum y_i K_i^{1/3}\right)^3$

The argon constants given by Zudkevitch and Kaufmann (106), and the nitrogen constants given by Crain and Sonntag (25) were used in this investigation (Table VI). Although the neon constants were found in recent publications (68), it was found that the equation with those constants deviates greatly from the experimental PvT behavior in the low temperature range up to about 120 K. Therefore, neon constants were calculated from the reduced constants, equation (3-20), and tested with the same data with the results much more reasonable (Table VI).

4. Strobridge Equation. The Strobridge equation (96) with 16 adjustable constants was originally developed for nitrogen and was influenced by the modified BWR equation developed by Bloomer and Rao (14). The Strobridge equation has the following form,

$$P = \frac{RT}{v} + \frac{S_1T+S_2+S_3/T+S_4/T^2+S_5/T^4}{v^2} +$$

$$\frac{S_6T+S_7}{v^3} + \frac{S_8T}{v^4} + \frac{S_9/T^2+S_{10}/T^3+S_{11}/T^4}{v^3} e^{-\frac{S_{16}}{v^2}} +$$

$$\frac{S_{12}/T^2+S_{13}/T^3+S_{14}/T^4}{v^5} e^{-\frac{S_{16}}{v^2}} + \frac{S_{15}}{v^6} \qquad (3\text{-}21)$$

where T is in K, v is in lit/mole, P is in atmospheres, R=0.0820574 $\frac{\text{lit-atm}}{\text{mole-K}}$ is the gas constant and S_1 through S_{16} are the constants of the Strobridge equation (Table VII). The constants S_1 through S_{15} are determined by least-squares fit and S_{16} by trial and error. Stewart and Timmerhaus (91) discussed the application of the Strobridge equation to the other cryogenic substances (helium, parahydrogen, argon, neon, and oxygen). The equation was found to represent the PvT behavior in both the vapor and liquid phases very accurately. The constants for argon (35), neon (51), and nitrogen (96) are shown in Table VII.

The equation was modified for neon by McCarty and Stewart (52), adding two more constants as follows:

$$P = \frac{RT}{v} + \frac{S_1T+S_2+S_3/T+S_4/T^2}{v^3} + \frac{S_5T^2+S_6T+S_7+S_8/T+S_9/T^2}{v^3}$$

$$+\frac{S_{10}T+S_{11}}{v^4} + \frac{S_{12}/T}{v^5} + \frac{S_{13}/T^2+S_{14}/T^3}{v^3} e^{-\frac{S_{18}}{v^2}}$$

$$+ \frac{S_{15}/T^2+S_{16}/T^3}{v^5} e^{-\frac{S_{18}}{v^2}} + \frac{S_{17}}{v^6} \qquad (3\text{-}22)$$

Later, Gibbons and Kuebler (34) redetermined the constants of the same equation for Neon (Table VIII).

TABLE VI

THE CONSTANTS OF THE BWR EQUATION

FOR ARGON, NEON AND NITROGEN

	Argon (106)	Neon (22)*	Nitrogen (25)
B_o	0.0222825	0.0180075	0.0281066
A_o	0.823408	0.144301	0.872086
C_o	13141.1	157.404	7813.75
b	0.00215287	0.000529716	0.0032351
a	0.0288353	0.00147	0.0312319
α	0.0000355384	0.0000052324	0.0000709232
c	798.231	3.22921	547.364
γ	0.002338	0.0010183	0.0045

Units: P - atm., v - liters/mole, T - K

R = 0.08207 lit. - atm./mole-K

* They are obtained from the reduced constants, equation (3-20)

TABLE VII

THE CONSTANTS OF THE STROBRIDGE EQUATION
FOR ARGON, NEON AND NITROGEN

	ARGON(35)	NEON(51)	NITROGEN(96)
R	0.08205348	0.08205736	0.08205736
S1	0.25978372E-02	0.15560398E-02	0.2766652498E-02
S2	-0.89735866E 00	-0.24655056E 00	-0.5771942735E 00
S3	-0.67273636E 02	0.43101692E 01	-0.1142108002E 03
S4	-0.26494175E 04	-0.16879375E 03	0.8522634277E 03
S5	0.97631230E 07	0.26561719E 05	0.3440176000E 07
S6	0.70478549E-04	0.53180513E-04	0.1354246488E-03
S7	-0.46767741E-02	-0.45629055E-03	-0.1578905806E-01
S8	0.22640761E-05	-0.67079094E-06	0.4168356099E-05
S9	0.48141064E 03	0.53957047E 02	0.3211547852E 03
S10	0.64565344E 05	-0.48134141E 04	0.1080120000E 06
S11	-0.11485282E 08	0.95157500E 05	-0.1066657800E 08
S12	-0.64835483E 00	-0.33474863E-01	-0.3304489136E 01
S13	0.46524805E 03	-0.96397638E 01	0.1223693604E 04
S14	0.10933574E 05	0.51358569E 03	-0.5693538672E 05
S15	0.69439528E-06	0.11034878E-07	0.1675166459E-05
S16	0.47999993E-02	0.63399971E-02	0.5599997938E-02

P : ATM. , V : LITERS/MOLE , T : K

TABLE VIII

THE CONSTANTS OF THE MODIFIED STROBRIDGE EQUATION FOR NEON (34)

R	0.08203524
S1	0.16937698E-02
S2	-0.17911500E 00
S3	-0.30956793E 01
S4	0.21567993E 01
S5	-0.10347196E-06
S6	0.41318499E-05
S7	0.27543299E-02
S8	0.89426696E-01
S9	-0.85555255E-01
S10	0.13340195E-05
S11	-0.13761700E-03
S12	-0.11055999E-04
S13	0.43160170E-02
S14	-0.12671199E 03
S15	-0.31678896E-01
S16	0.14593992E 01
S17	0.23412198E-07
S18	0.27957298E-02

P : ATM. , V : LITERS/MOLE , T : K

Crain and Sonntag (24) applied the equation to argon-nitrogen systems with their new experimental PvT data for three different compositions. They also determined the argon-nitrogen interaction constants besides determining new constants for the pure components. Then, Crain and Sonntag and others (87) tried to extend the Strobridge equation to different binary mixtures; however, no reasonable combining rules could be determined. Besides these studies, no other application of the Strobridge equation to mixtures was found.

5. Martin's Equation. The original Martin-Hou (MH) equation with 10 constants (59) may be written as,

$$P = \sum_{i=1}^{5} \frac{f_i(T)}{(v-b)^i} \qquad (3\text{-}23)$$

where

$$f_i(T) = a_i + b_i T + c_i e^{-kT} \qquad (3\text{-}23a)$$

$$a_1 = c_1 = 0$$

$$b_4 = c_4 = 0$$

$$a_5 = c_5 = 0$$

and $b_1 = R$ is the gas constant. Then, in 1959, the constants a_5 and c_5 were added (60). Although the constants of the original equation had been determined for seven different gases, the constants of the modified equation were obtained only for carbon-dioxide (60) and nitrogen (85). The MH equation is capable of precisely representing the PvT behavior of gases up to about 1.5 times critical density.

In 1962, a slightly different equation,

$$f_i(T) = a_i + b_i T + c_i e^{k/T} \qquad (3\text{-}24a)$$

instead of equation (3-23a), was proposed by Martin (58).

Later, Martin improved the equation for the high density region by adding two exponential terms as follows (57)

$$P = \sum_{i=1}^{7} \frac{f_i(T)}{g_i(v)} \tag{3-25}$$

where

$$f_i(T) = a_i + b_i T + c_i e^{-kT} \qquad i = 1, \ldots, 7 \tag{3-25a}$$

$$g_i(v) = \begin{cases} (v-b)^i & i = 1, \ldots, 5 \\ e^{\alpha_i v} & i = 6, 7 \end{cases} \tag{3-25b}$$

$a_1 = c_1 = 0$, $b_1 = R$ is the gas constant and

a_i, b_i, c_i ($i = 2, \ldots, 7$), α_6, α_7 ($\alpha_7 = 2 \cdot \alpha_6$), k, and b are the constants of the equation. This equation may be arranged as follows:

$$P = A(v) + B(v) \cdot T + C(v) \cdot e^{-kT} \tag{3-26}$$

where

$$A(v) = \sum_{i=1}^{7} \frac{a_i}{g_i(v)} \tag{3-26a}$$

$$B(v) = \sum_{i=1}^{7} \frac{b_i}{g_i(v)} \tag{3-26b}$$

$$C(v) = \sum_{i=1}^{7} \frac{c_i}{g_i(v)} \tag{3-26c}$$

This equation was applied to chlorodifluoromethane with 16 constants ($c_4=c_6=a_7=b_7=c_7=0$) and to carbon-dioxide only for the critical isotherm with better precision up to 2 times critical density. Although the Martin equation does not represent the PvT behavior of the pure substances as accurately as the Strobridge equation, because the constants of the Martin equation are determined by means of general behavior of substances, its

application to mxitures may produce better results with reasonable combining rules.

Smith, Sonntag, and Van Wylen tested several combining rules for the original equation (3-23) with 10 constants and twelve constants (85,86). The suggested combining rules, as shown in Table IX, were only tested for the carbon-dioxide-nitrogen system.

TABLE IX

THE COMBINING RULES OF THE CONSTANTS

OF THE MH EQUATION (85)

Constants	Combining Rules
b	$K_m = \sum_i y_i K_i$
b_2, b_3, b_5, T_c	$K_m = (\sum_i y_i K_i^{1/2})^2$
$a_2, a_3, a_4, a_5, c_2, c_3, c_5$	$K_m = \sum_i \sum_j y_i y_j (\frac{K_i^{1/3} + K_j^{1/3}}{2})^3$

Since that time, no application of either the former (3-23) or the latter (3-25) equation for mixtures has been found.

Martin has recently (1972) been investigating a new form of the equation as follows:

$$P = \frac{RT}{(v-b)} + \frac{f_2(T)}{(v-b)(v-t)} + \frac{f_3(T)}{(v-b)^3} + \frac{f_4(T)}{(v-b)^4} + \frac{f_5(T)}{e^{av}(1+ce^{av})} + \frac{f_6(T)}{e^{2av}(1+de^{2av})} \qquad (3\text{-}27)$$

where

$$f_i(T) = a_i + b_iT + c_ie^{-kT} \qquad (3\text{-}27a)$$

However, the investigation is not yet complete.

6. The Modified Martin Equation. The form of Martin's recent equation (3-25) was the one considered for the prediction of the PvT behavior of mixtures; however, there was no application to argon, neon, and nitrogen. Therefore, it was necessary to determine the constants for those pure substances whose mixtures would be studied.

At the beginning the modification that $b = 0$ would always be assumed was considered. To use $b \neq 0$ was perhaps necessary for the original MH equation (3-23) in order to have an infinite series in density, but the two exponential terms of the recent Martin equation (3-25) might be able to represent the infinite series.

Consider the expansions of $1/(v-b)^i$, $i = 1,\ldots,5$

$$\frac{1}{v-b} = \frac{1}{v}\left(1 + \frac{b}{v} + \frac{b^2}{v^2} + \ldots\right) = \frac{1}{v}\sum_{n=o}^{\infty}\left(\frac{b}{v}\right)^n$$

$$\frac{1}{(v-b)^2} = \frac{d}{db}\left(\frac{1}{v-b}\right) = \frac{1}{v^2}\sum_{n=o}^{\infty}(n+1)\left(\frac{b}{v}\right)^n$$

.....

$$\frac{1}{(v-b)^m} = \frac{d^{m-1}}{db^{m-1}}\left(\frac{1}{v-b}\right) = \frac{1}{v^m}\sum_{n=o}^{\infty}\binom{n+m-1}{n}\left(\frac{b}{v}\right)^n \qquad (3\text{-}28)$$

where $\binom{n+m-1}{n}$ is the binomial coefficient.

Substituting the equation (3-28) into (3-23) and the MH equation may be written as

$$P = \sum_{i=1}^{5}\frac{f_i(T)}{(v-b)^i} = \sum_{i=1}^{5}\frac{\Theta_i(T)}{v^i} + G(T,v) \qquad (3\text{-}29)$$

where

$$\Theta_1(T)=f_1(T)=RT$$

$$\Theta_2(T)=bf_1(T) + f_2(T)$$

$$\Theta_3(T)=b^2f_1(T) + 2bf_2(T) + f_3(T)$$

$$\Theta_4(T)=b^3f_1(T) + 3b^2f_2(T) + 3bf_3(T) + f_4(T)$$

$$\Theta_5(T)=b^4f_1(T)+4b^3f_2(T) +6b^2f_3(T) + 4bf_4(T) + f_5(T) \qquad (3\text{-}30)$$

$$G(T,v) = \sum_{i=6}^{\infty} \frac{\Theta_i(T)}{v^i} \qquad (3\text{-}31)$$

$$\Theta_i(T) = \sum_{j=1}^{5} \binom{i-1}{j-1} b^{i-1} f_j(T), \quad i = 6,7,... \qquad (3\text{-}32)$$

Consequently, instead of adding those two exponential terms to the equation (3-23) in order to obtain the equation (3-25) G(T,v) is replaced with them. Thus, the equation of state may be written as follows

$$P_r = \sum_{i=1}^{7} \frac{\Theta_i(T)}{\varphi_i(v)} \qquad (3\text{-}33)$$

where

$$\Theta_i(T) = A_i + B_iT + C_ie^{-k(\frac{T}{Tc} -1)} \qquad i = 1, \ldots, 7 \qquad (3\text{-}33a)$$

$$\varphi_i(v) = \begin{cases} v^i & i=1,\ldots,5 \\ e^{\alpha_i(v-v_c)} & i=6,7 \end{cases} \qquad (3\text{-}33b)$$

$A_1 = C_1 = 0$, $B_1 = R$ is the gas constant and A_i, B_i, C_i $(i=2,\ldots,7)$, α_6, α_7, k are the 21 constants of the equation. To write the equation in reduced form may be considered more convenient, therefore,

$$P_r = \sum_{i=1}^{7} \frac{\tau_i(T_r)}{\Phi_i(v_r)} \qquad (3\text{-}34)$$

where

$$P_r = P/P_c, \quad v_r = v/v_c, \quad T_r = T/T_c \quad \text{and}$$

$$\tau_i(T_r) = A_{ri} + B_{ri}T_r + C_{ri}\, e^{-k(T_r-1)} \tag{3-34a}$$

$$\Phi_i(v_r) = \begin{cases} v_r^i & i=1,\ldots,7 \\ e^{\alpha_{ri}(v_r-1)} & i=1,\ldots,5 \\ & i=6,7 \end{cases} \tag{3-34b}$$

$A_{r1} = C_{r1} = 0$, $B_{r1} = 1/Z_c$ and $Z_c = P_c v_c/RT_c$ is the critical compressibility.

The relation between the constants of the former equation (3-33) and the latter equation (3-34) may be given by

$$A_{ri} = \frac{A_i}{P_c v_c^{\,i}}, \quad B_{ri} = \frac{B_i T_c}{P_c v_c^{\,i}}, \quad C_{ri} = \frac{C_i}{P_c v_c^{\,i}} \quad i=1,\ldots,5 \tag{3-35a}$$

$$A_{ri} = \frac{A_i}{P_c}, \quad B_{ri} = \frac{B_i T_c}{P_c}, \quad C_{ri} = \frac{C_i}{P_c} \quad i = 6,7 \tag{3-35b}$$

$$\alpha_{r6} = \alpha_6 v_c, \quad \alpha_{r7} = \alpha_7 v_c \tag{3-35c}$$

This form of the equation (3-34) is first tested with carbon-dioxide for the critical isotherm in order to compare this equation with equation (3-25). (Table X).

B. GENERAL BEHAVIOR OF SUBSTANCES

1. The Critical State. The critical state of a pure substance, from the classical viewpoint, may be considered as the state at which, when the vapor of that substance is compressed at a certain minimum temperature (or is cooled at a certain minimum pressure) condensation does not occur, but that isotherm (or that constant pressure curve) displays

TABLE X

A COMPARISON OF THE MARTIN (3-24) AND THE MODIFIED MARTIN (3-33)

EQUATIONS FOR THE CRITICAL ISOTHERM OF CARBON-DIOXIDE

v cc/mole	P_{exp} atm.	P_{cal} atm.	Dev. % (Eqn. 3-33)	Dev. % (57) (Eqn. 3-24)
37.336	1417.397	1416.830	-0.04	-4.46
39.533	942.151	955.802	1.45	-2.06
42.234	586.800	599.333	2.14	0.47
45.276	359.956	366.371	1.78	2.14
48.729	221.966	223.339	0.62	2.33
52.739	142.461	141.394	-0.75	-0.99
57.581	99.925	98.802	-1.12	-0.43
63.234	81.260	80.850	-0.50	-0.61
94.065	72.850	72.850	-0.00	0.00
130.659	72.326	72.284	-0.06	-0.09
144.800	71.564	71.539	-0.04	-0.10
166.844	69.795	69.792	-0.00	-0.12
198.513	66.447	66.485	0.06	-0.09
244.414	61.101	61.149	0.08	-0.04
322.024	52.734	52.763	0.06	0.00
428.934	43.725	43.732	0.01	0.02
472.579	40.784	40.787	0.01	0.03
486.623	39.912	39.916	0.01	0.03
524.934	37.704	37.705	0.00	0.04
591.884	34.353	34.352	-0.00	0.04
679.309	30.755	30.750	-0.02	0.04
790.370	27.116	27.112	-0.01	0.05
949.198	23.173	23.169	-0.02	0.05
1187.699	19.002	19.000	-0.01	0.05

a horizontal inflection point on the P-v (or the T-v) plot (Figure 1). The temperature, the pressure, and the specific volume at the horizontal inflection point on either the P-v or the T-v diagram are called, as is well known, the critical constants of the pure substances. The methods and apparatus used for the determination of the critical constants have been discussed by several authors (44, 48, 76).

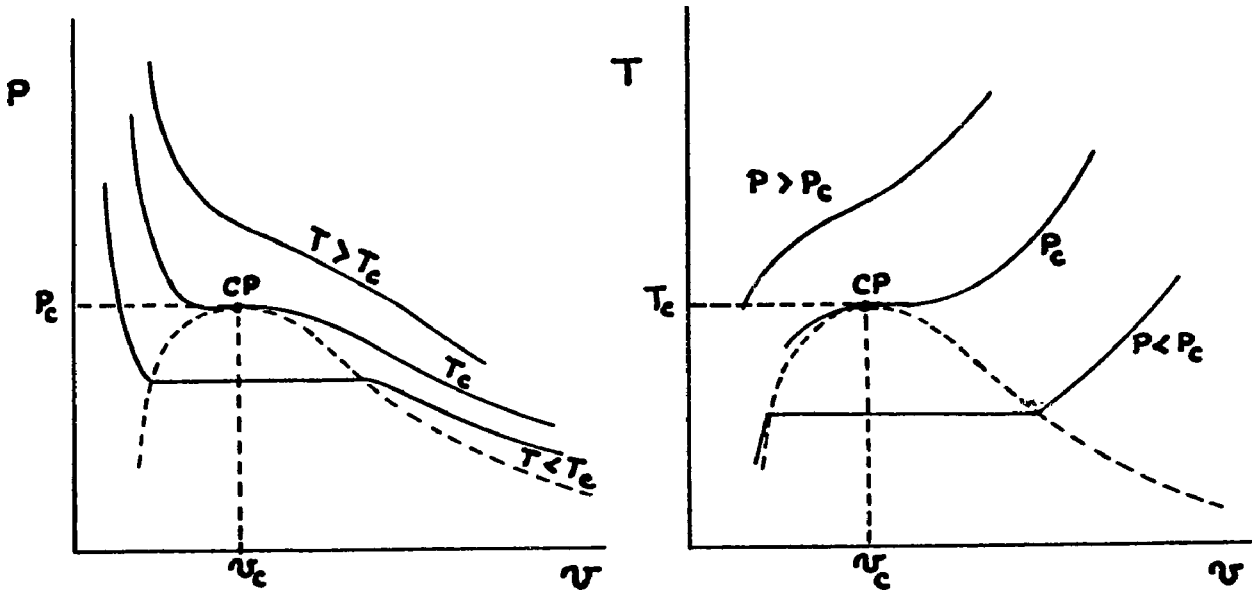


Figure 1. The critical state of pure substances

On the other hand, the critical state for mixtures designates more complex behavior. However, we may describe the critical state for mixtures in a similar manner as that of pure substances. When a gas mixture is compressed at a certain minimum temperature, condensation may start but cannot be completed and the isotherm passes through two dew points (retrograde behavior of the first kind), or, when heat is rejected from the same gas mixture at a certain minimum pressure the similar behavior may occur and the isobar passes through two bubble points (retrograde behavior of the second kind). This point is generally called the true

critical point or the critical point of the mixture whose composition is invariable (Figure 2). From vapor-liquid behavior, the true critical state of a mixture may be considered as the state that represents maximum pressure and temperature at which two phases may exist. Rowlinson (80) gives a very clear discussion about the true critical state of mixtures. Reid and Sherwood (76) give a summary of the estimation technique of the true critical temperatures and pressures of mixtures.

The critical state behavior of pure substances gives two well-known, analytical thermodynamic relations, as follows:

$$\left(\frac{\partial P_r}{\partial v_r}\right)_{\substack{T_r=1 \\ \text{at } v_r=1}} = \frac{v_c}{P_c}\left(\frac{\partial P}{\partial v}\right)_{\substack{T_c \\ \text{at } v_c}} = 0 \qquad (3\text{-}36)$$

$$\left(\frac{\partial^2 P_r}{\partial v_r^2}\right)_{\substack{T_r=1 \\ \text{at } v_r=1}} = \frac{v_c^2}{P_c}\left(\frac{\partial^2 P}{\partial v^2}\right)_{\substack{T_c \\ \text{at } v_c}} = 0 \qquad (3\text{-}37)$$

The higher order, such as third and fourth, derivatives of pressure with respect to volume along the critical isotherm at the critical point are most often assumed negligible: however, it is very likely that the values of the third and fourth derivatives at the critical point are small negative and small positive, respectively. The first and second derivatives at the critical point, equations (3-36) and (3-37), imply that the value of the third derivative, even near the critical point, can, indeed, not be positive. When the third derivative is zero, the fourth derivative must be zero mathematically (a). In addition, for this situation, the second derivative must have a horizontal inflection point at the critical specific volume so that the critical isotherm should be flatter than the

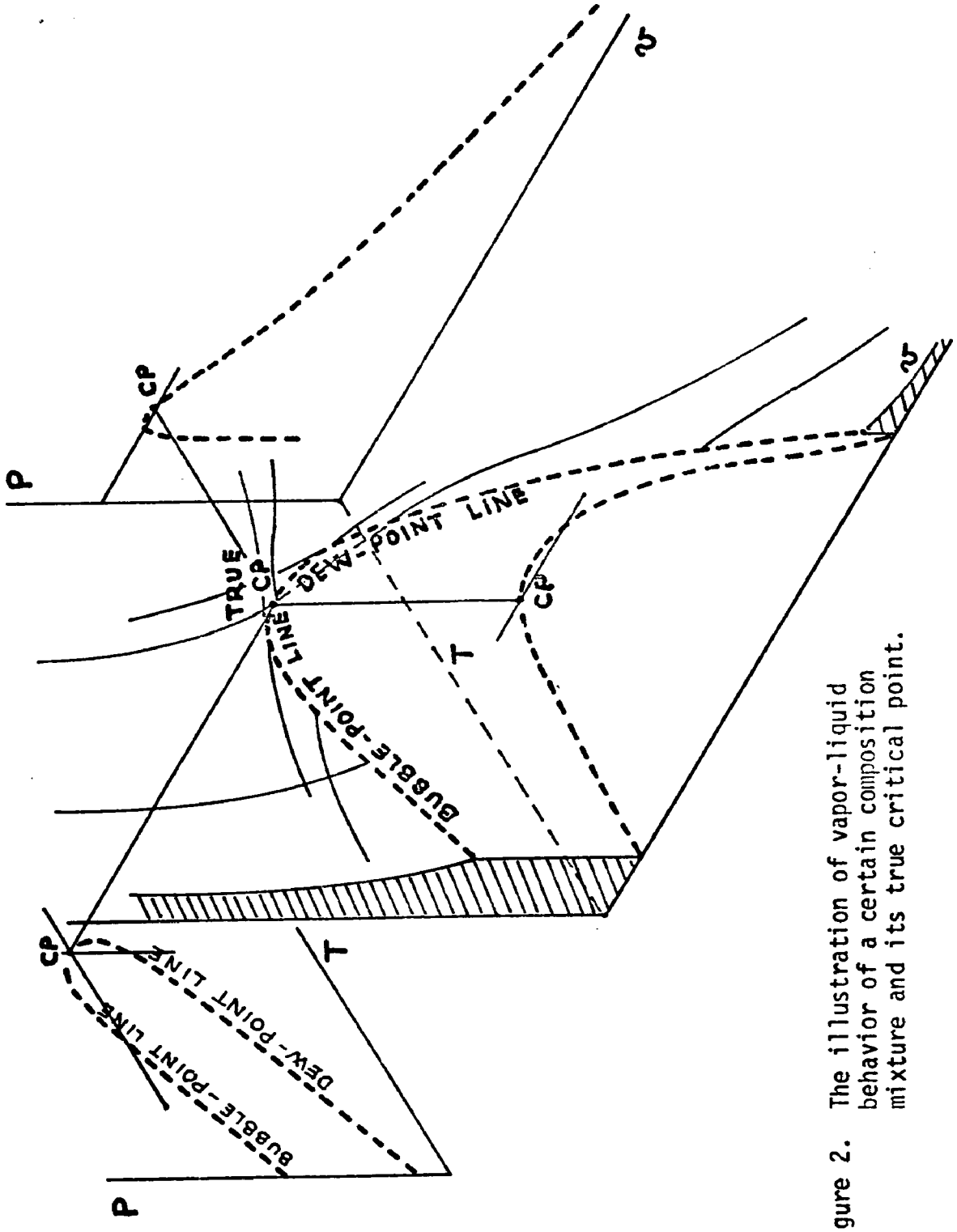


Figure 2. The illustration of vapor-liquid behavior of a certain composition mixture and its true critical point.

real behavior in the critical region (Figure 3 a). When the third derivative is slightly negative at the critical specific volume, three arguments may be deduced: that the fourth derivative is negative (b), zero (c), or positive (d) (Figure 3). The first argument, that the fourth derivative is negative implies that the third derivative must have a horizontal inflection point at the specific volume less than the critical. So, this makes the critical isotherm at the same region much flatter than is actual (Figure 3b). The other argument, that the fourth derivative is zero when the third is negative gives almost the same result, less flat and closer to real behavior (Figure 3c). Martin usually suggests this possibility and used it in his work (57,59). The last argument, that the third derivative is negative and that the fourth is positive may be regarded as a comprehensive possibility and also includes the other arguments (a) and (c).

Although the numerical values of the third and fourth derivatives at the critical point are very small, they of course, depend on the unit system. The reduced derivatives (the derivatives of the reduced pressure with respect to reduced volume along the critical isotherm) perhaps can be taken into consideration as an essential outcome. Consequently, the values of the reduced third and fourth derivatives cannot, as shown in the following relations, be assumed to be negligible.

$$\left(\frac{\partial^3 P_r}{\partial v_r^3}\right)_{\substack{T_r=1 \\ \text{at } v_r=1}} = \frac{v_c^3}{P_c}\left(\frac{\partial^3 P}{\partial v^3}\right)_{\substack{T_c \\ \text{at } v_c}} = -\varepsilon_3 \qquad (3\text{-}38)$$

$$\left(\frac{\partial^4 P_r}{\partial v_r^4}\right)_{\substack{T_r=1 \\ \text{at } v_r=1}} = \frac{v_c^4}{P_c}\left(\frac{\partial^4 P}{\partial v^4}\right)_{\substack{T_c \\ \text{at } v_c}} = \varepsilon_4 \qquad (3\text{-}39)$$

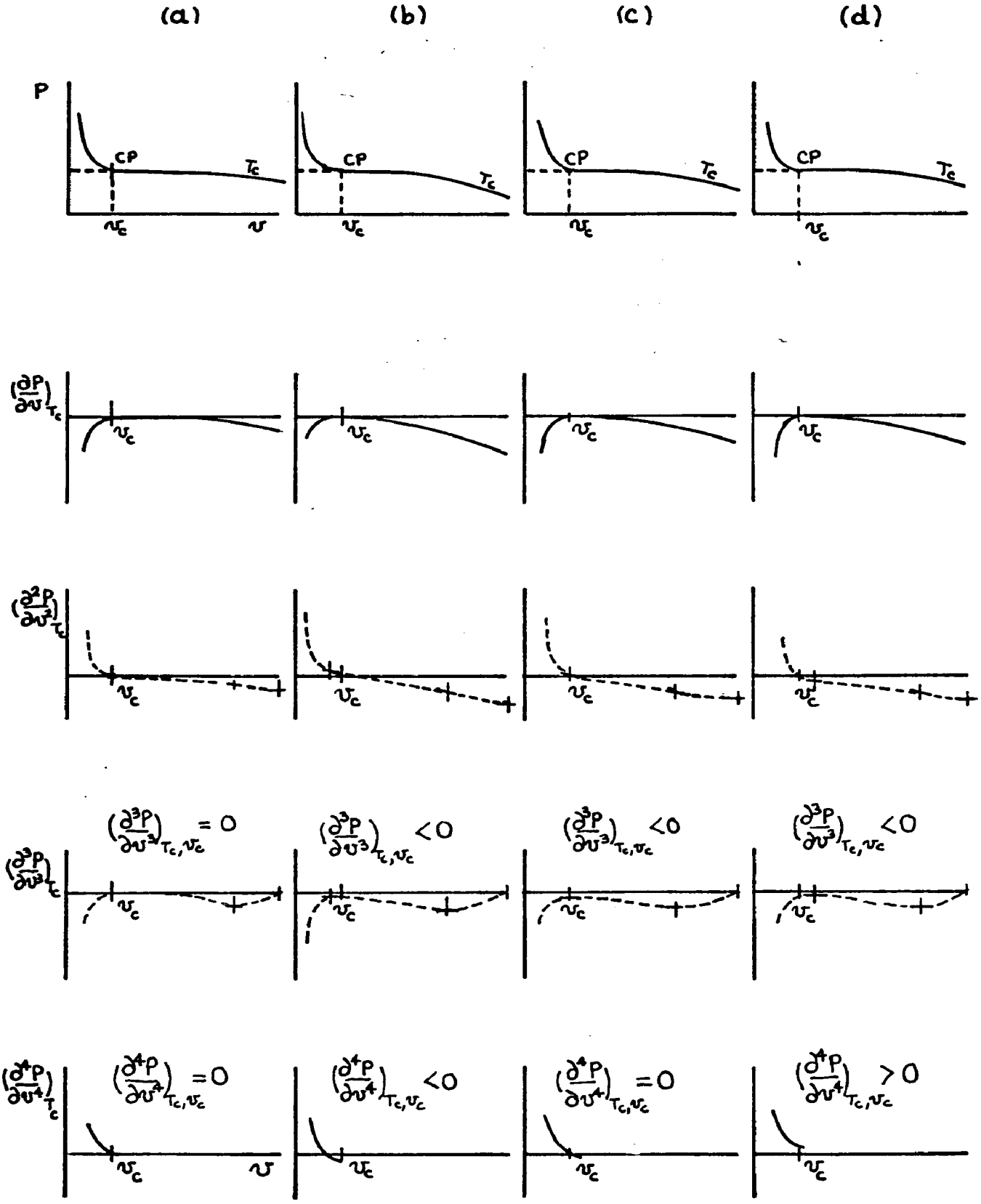


Figure 3. The derivatives of the critical isotherms

Those values determined for argon, neon, nitrogen, and carbon-dioxide from their experimental PvT data of the critical isotherms with the method of successive approach are listed in Table XI. If the reduced isotherms of those substances for the higher than the critical density are plotted on the P_v-v_r diagram, as shown in Figure 4, the agreement between the numerical values (Table XI) and the curves is evident. Given these circumstances, the isotherms of carbon-dioxide and nitrogen are flatter than the isotherms of argon and neon and so the former substances have smaller numerical values for ε_3 and ε_4 than the latter.

TABLE XI

THE NUMERICAL VALUES OF THE THIRD AND FOURTH DERIVATIVES OF THE REDUCED PRESSURE WITH RESPECT TO REDUCED SPECIFIC VOLUME AT THE CRITICAL POINT

	$\left(\frac{\partial^3 P_r}{\partial v_r^3}\right)_{\substack{T_r=1 \\ \text{at } v_r=1}} = -\varepsilon_3$	$\left(\frac{\partial^4 P_r}{\partial v_r^4}\right)_{\substack{T_r=1 \\ \text{at } v_r=1}} = \varepsilon_4$
Argon	-2.56	40.3
Neon	-2.77	41.3
Nitrogen	-1.91	27.3
Carbon-Dioxide (approximately)	-1.43	20.8

2. Second Virial Coefficient. From the PvT behavior of gases it may be observed that, as the pressure approaches zero (for which the specific volume becomes indefinitely large) the compressibility factor ($Z=Pv/RT$) for all isotherms approaches unity. This may be expressed by

$$\lim_{P \to 0} Z = 1 \qquad (3\text{-}40)$$

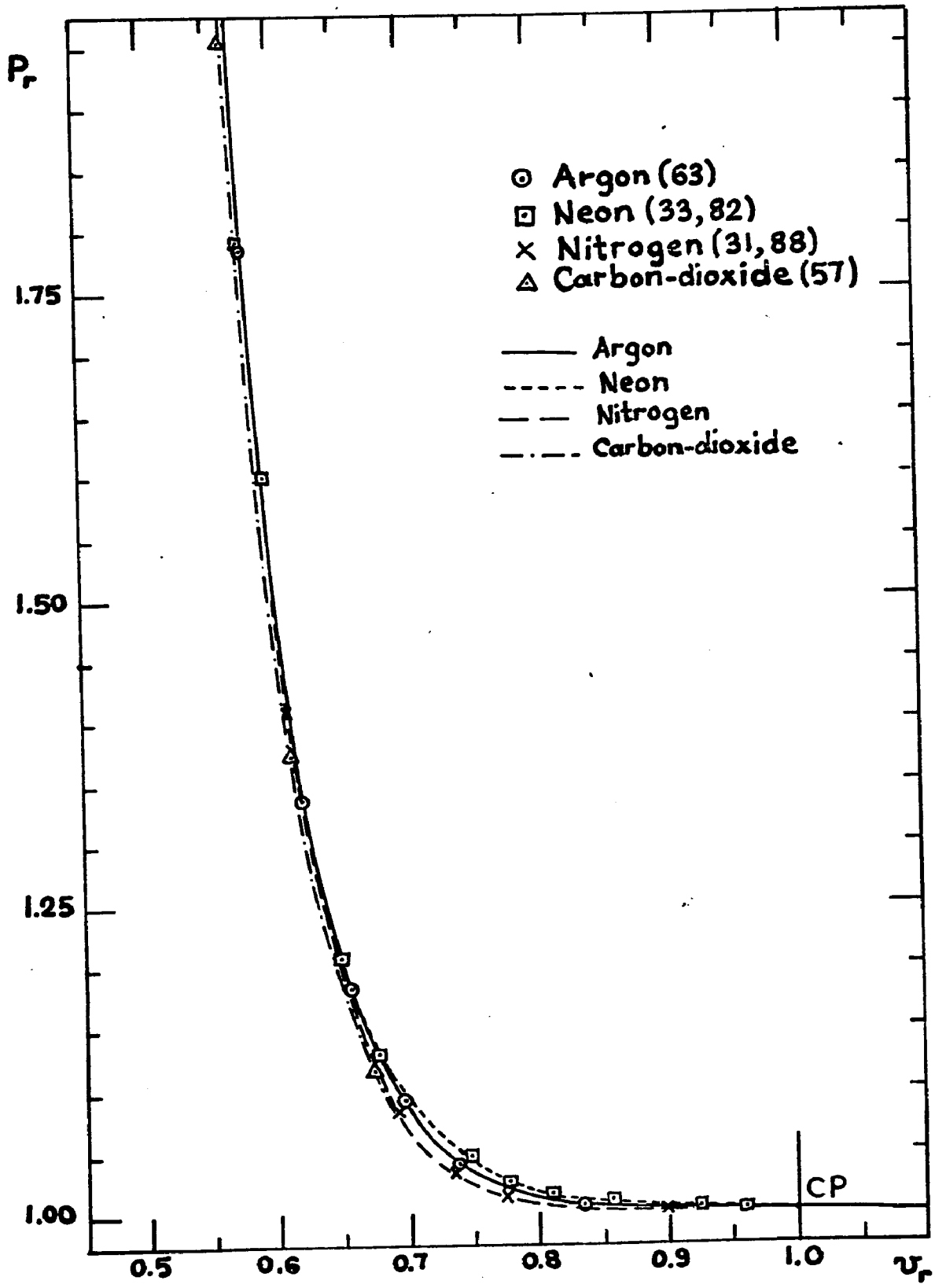


Figure 4. Comparison of the critical isotherms of argon, neon, nitrogen and carbon dioxide at higher than critical density

When this behavior, ideal gas behavior, is indicated on the Z-P or the Z-(1/v) diagram, it is obvious that the compressibility for each isotherm approaches unity with a different slope as shown in Figure 5. The slopes of the isotherms at zero pressure or infinite volume on the Z-P or the Z-(1/v) diagram may be defined as the second virial coefficient B' or B, respectively.

$$B' = \lim_{P \to 0} \left(\frac{\partial Z}{\partial P}\right)_T \tag{3-41}$$

$$B = \lim_{v \to \infty} \left(\frac{\partial Z}{\partial (1/v)}\right)_T \tag{3-42}$$

The relation between B and B' can be determined mathematically as follows:

$$\left(\frac{\partial Z}{\partial P}\right)_T = \left(\frac{\partial Z}{\partial (1/v)}\right)_T \left(\frac{\partial (1/v)}{\partial P}\right)_T = \left(\frac{\partial Z}{\partial (1/v)}\right)_T \left[\frac{1}{ZRT} - \frac{P}{Z^2 RT}\left(\frac{\partial Z}{\partial P}\right)_T\right] \tag{3-43}$$

As $P \to 0$ (and $v \to \infty$) the left side of the equation (3-43) approaches B' and the first and second terms of the right side approach

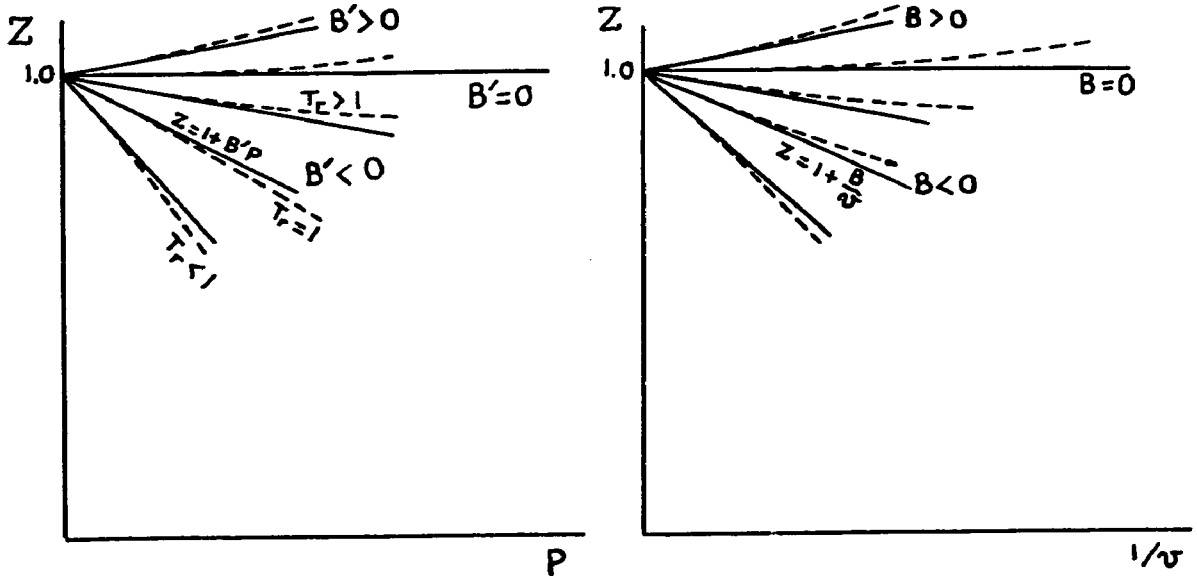


Figure 5. Compressibility diagram at low pressure

B/RT and zero respectively. Then,

$$B' = \frac{B}{RT} \tag{3-44}$$

is obtained. Evidently, each isotherm at zero pressure (or infinite specific volume) has a different slope and, consequently, it can be concluded that the second virial coefficient is the function of temperature only. This characteristic of the second virial coefficient is also derived from statistical thermodynamics by correlating the intermolecular force as a two-particle interaction. Several texts (42,44,77,89) discuss this evaluation, and it is not necessary to repeat it here.

Except at high temperatures, the second virial coefficient is negative. At the temperature which is called the Boyle temperature, the second virial coefficient is zero, and at any temperature exceeding the Boyle temperature the second virial coefficient is positive (Figure 6). The reduced Boyle temperature is about 2.5 for most substances, about 3.3 for hydrogen, and about 2.1 for water. Martin discussed a correlation between the Boyle temperature and the critical temperature (59). At a temperature about 5 times the critical temperature the second virial coefficient has a maximum value.

The reduced second virial coefficients may be described as follows:

$$B_r = \frac{B}{v_c} \quad \text{or} \quad B'_r = B'P_c \tag{3-45}$$

The relation between B_r and B'_r may be obtained from equation 3-44, as

$$B'_r = B_r \frac{Z_c}{T_r} \tag{3-46}$$

To use the second virial coefficient in reduced form is usually more convenient and more rational because the curves of the reduced second

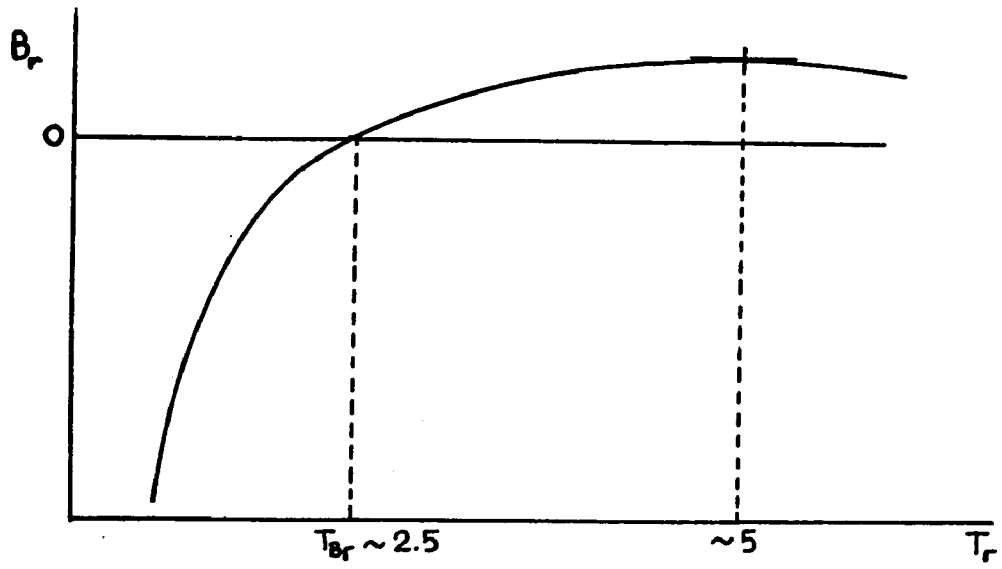


Figure 6. The reduced second virial coefficient

virial coefficients for different substances are in point of fact near each other. Therefore, several investigators attempted to fit an algebraic relation empirically to the reduced second virial coefficients as follows:

$$B_r' = \frac{0.18764}{T_r} - \frac{0.4758}{T_r^2} - \frac{0.05}{T_r^4} \quad (4) \qquad (3\text{-}47)$$

$$B_r' = \frac{0.188}{T_r} - \frac{0.468}{T_r^2} - \frac{8.87}{T_r^2} e^{-5T_r} \quad (56) \qquad (3\text{-}48)$$

$$B_r = 0.430 - \frac{0.886}{T_r} - \frac{0.694}{T_r^2} \quad (55) \qquad (3\text{-}49)$$

On the other hand, different correlations are used in the equations of state to represent the second virial coefficients. The equation which is similar to equation (3-47) and is used in the BWR equation (3-18) is,

$$B = B_o - \frac{A_o}{RT} - \frac{C_o}{RT^3} \qquad (3\text{-}50)$$

The second virial coefficient of the Strobridge equation (3-21) is,

$$B = \frac{S_1}{R} + \frac{S_2}{RT} + \frac{S_3}{RT^2} + \frac{S_4}{RT^3} + \frac{S_5}{RT^5} \qquad (3\text{-}51)$$

and the equation which is a combination of the equations (3-47) and (3-49) in form is used by McCarty and Stewart in the modified Strobridge equation (3-22),

$$B = \frac{S_1}{R} + \frac{S_2}{RT} + \frac{S_3}{RT^2} + \frac{S_4}{RT^3} \tag{3-52}$$

The second virial coefficients calculated from the MH (3-23) and the Martin (3-25) equations are the same:

$$B = \frac{a_2}{RT} + (b + \frac{b_2}{R}) + \frac{c_2}{RT} e^{-kT} \tag{3-53}$$

In 1963 Martin suggested a slightly different form of equation,

$$B = \frac{a_2}{RT} + (b + \frac{b_2}{R}) + \frac{c_2}{RT} e^{k/T} \tag{3-54}$$

and in this work an equation similar to equation (3-48) was used:

$$B_r = \frac{A_{r_2} Z_c}{T_r} + B_{r_2} Z_c + \frac{C_{r_2} Z_c}{T_r} e^{-k(T_r-1)} \tag{3-55}$$

3. Third Virial Coefficient. By the same consideration as the second virial coefficient, the third virial coefficient may be defined as

$$C' = \lim_{P \to 0} \frac{1}{2} \left(\frac{\partial^2 Z}{\partial P^2}\right)_T \tag{3-56}$$

$$C = \lim_{v \to \infty} \frac{1}{2} \left(\frac{\partial^2 Z}{\partial (1/v)^2}\right)_T \tag{3-57}$$

On the Z-P or Z-(1/v) diagram, the half values of the curvatures of isotherms, which are the second derivatives of compressibility with respect to pressure or density, at zero pressure or infinite specific volume give the third virial coefficient as a function of temperature only. The correlation between C and C' can be obtained algebraically as follows:

$$\left(\frac{\partial^2 Z}{\partial P^2}\right)_T = \frac{\partial}{\partial P}\left(\frac{\partial Z}{\partial P}\right)_T = \frac{\partial}{\partial P}\left[\left(\frac{\partial (1/v)}{\partial P}\right)_T \cdot \left(\frac{\partial Z}{\partial (1/v)}\right)_T\right] \tag{3-58}$$

Then, the following may be written,

$$\left(\frac{\partial^2 Z}{\partial P^2}\right)_T = \left[\left(\frac{\partial (1/v)}{\partial P}\right)_T\right]^2 \cdot \left(\frac{\partial^2 Z}{\partial (1/v)^2}\right)_T + \left(\frac{\partial^2 (1/v)}{\partial P^2}\right)_T \cdot \left(\frac{\partial Z}{\partial (1/v)}\right)_T \tag{3-59}$$

or, on the other hand,

$$\left(\frac{\partial (1/v)}{\partial P}\right)_T = \frac{1}{ZRT} - \frac{P}{Z^2 RT}\left(\frac{\partial Z}{\partial P}\right)_T \tag{3-60}$$

$$\left(\frac{\partial^2 (1/v)}{\partial P^2}\right)_T = -\frac{2}{Z^2 RT}\left(\frac{\partial Z}{\partial P}\right)_T + \frac{2P}{Z^3 RT}\left[\left(\frac{\partial Z}{\partial P}\right)_T\right]^2 - \frac{P}{Z^2 RT}\left(\frac{\partial^2 Z}{\partial P^2}\right)_T \tag{3-61}$$

Substituting equations (3-60) and (3-61) into equation (3-59) and taking the limit as $P \rightarrow 0$ (or $v \rightarrow \infty$), Z approaches unity and the terms which include P become zero; then,

$$C' = \frac{C - B^2}{(RT)^2} \tag{3-62}$$

The third virial coefficient may also be reduced as,

$$C'_r = C' P_c^2 \tag{3-63}$$

$$C_r = \frac{C}{v_c^2} \tag{3-64}$$

and then the relation between C'_r and C_r is obtained by substituting equations (3-63) and (3-64) into (3-62)

$$C'_r = (C_r - B_r^2)\left(\frac{Z_c}{T_r}\right)^2 \tag{3-65}$$

Although there is an abundance of experimental and theoretical studies on the second virial coefficient, much less work has been done on the third virial coefficient. However, it is possible to find some correlation in order to understand its behavior.

Chueh and Prausnitz, in 1967, collected the experimental third virial coefficient data available for nonpolar gases including the quantum gases helium, hydrogen, and neon (19). The plot of the reduced third virial coefficient, C_r, against the reduced temperature, T_r, shows that the curves of different gases separate from each other by reaching a maximum at about 0.85-0.9 of reduced temperature and coincide with each other for reduced temperatures greater than 1.75 and then decrease through a positive value as the temperature is further increased (Figure 7). The experimental data having such a maximum value is fairly well in agreement with the theoretical approach (44,76). Then, Chueh and Prausnitz derived an equation empirically for the reduced third virial coefficient as follows (19),

$$C_r = \left(\frac{0.232}{T_r^{0.25}} + \frac{0.468}{T_r^{5}}\right)\left(1 - e^{(1-1.89T_r^2)}\right) + \Delta C_r \qquad (3\text{-}66)$$

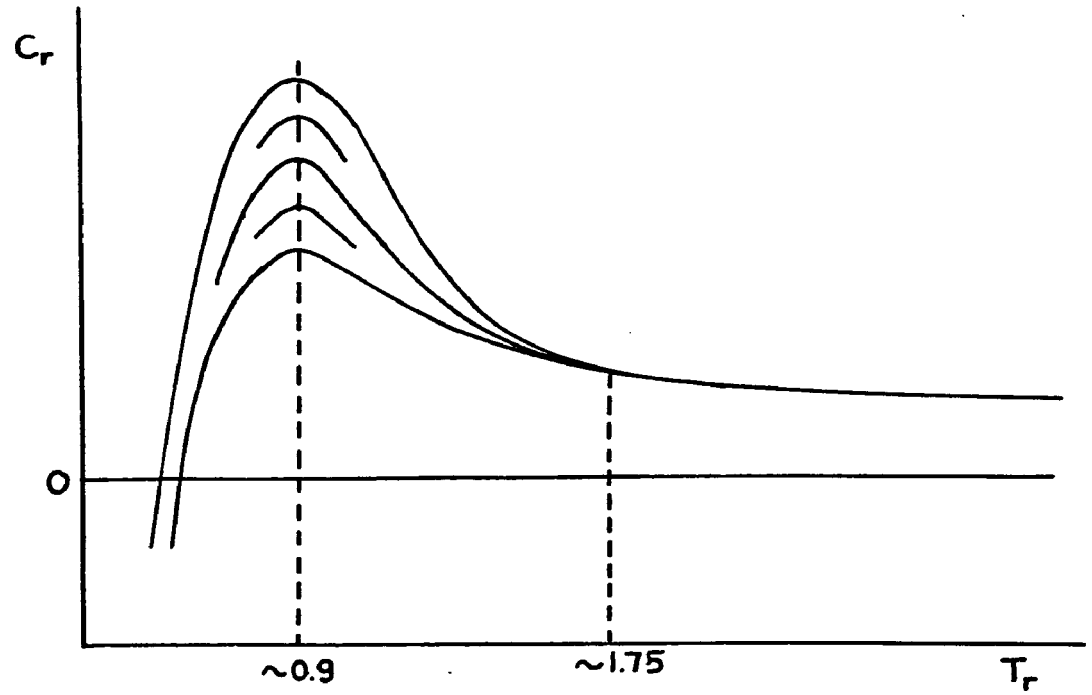


Figure 7. The reduced third virial coefficient

where ΔC_r is a deviation function and approaches zero for $T_r > 1.75$. This equation is more complicated than the relations used in the equations of state to represent the third virial coefficient and those relations are listed as follows:

In the BWR equation of state (3-18),

$$C = b - \frac{a}{RT} - \frac{C}{RT^3} \tag{3-67}$$

in the Strobridge equation of state (3-21),

$$C = \frac{S_6}{R} + \frac{S_7}{RT} + \frac{S_9}{RT^3} + \frac{S_{10}}{RT^4} + \frac{S_{11}}{RT^5} \tag{3-68}$$

in the modified Strobridge equation (by McCarty and Stewart) (3-22):

$$C = \frac{S_5 T}{R} + \frac{S_6}{R} + \frac{S_7}{RT} + \frac{S_8}{RT^2} + \frac{S_9+S_{13}}{RT^3} + \frac{S_{14}}{RT^4} \tag{3-69}$$

The third virial coefficient of the Martin equation (3-25) is,

$$C = \frac{2ba_2+a_3}{RT} + \left(b^2 + \frac{2bb_2+b_3}{R}\right) + \frac{2bc_2 + c_3}{RT} e^{-kT} \tag{3-70}$$

which is the same in form as for the second virial coefficient. Even for the higher order virial coefficients, the equations are obtained in the same manner. In this work, also, similar forms of relations for the third and higher order virial coefficients were used,

$$C_r = \frac{A_{r3}Z_c}{T_r} + B_{r3}Z_c + \frac{C_{r3}Z_c}{T_r} e^{-k(T_r-1)} \tag{3-71}$$

$$D_r = \frac{A_{r4}Z_c}{T_r} + B_{r4}Z_c + \frac{C_{r4}Z_c}{T_r} e^{-k(T_r-1)} \tag{3-72}$$

and so forth.

4. The Nature of Isometrics. The plot of P_r against T_r along the lines of the constant specific volume - that is, isometric lines - shows the other important characteristic of substances. Early investigators

considered that these isometrics have a linear behavior. It is indeed true that the isometrics are very close to straight lines.

The behavior of the isometrics may be understood by the slope of isometrics which is called the thermal-pressure coefficient (80), $(\partial P_r/\partial T_r)_{v_r} = \gamma_{rv}$, and by the curvature, that is, $(\partial^2 P_r/\partial T_r^2)_{v_r}$, of the isometrics on the P_r vs T_r plot. These characteristics were thoroughly summarized by Martin (59) and Rowlinson (80).

An observation along an isotherm near the critical temperature shows that the curvatures of isometrics change signs twice; such that, it is negative below about critical density; it is positive between the critical density and about 1.8 or 2.0 times critical density; then it becomes negative again.

This is fairly consistent with the slope of the constant-volume specific heat with respect to specific volume at constant temperature. The constant volume specific heat changes with specific volume at a temperature near the critical such that it passes through a maximum at the critical density after having a minimum at about 1.8 or 2.0 times critical density (Figure 8). Recalling the thermodynamic relation

$$\left(\frac{\partial^2 P_r}{\partial T_r^2}\right)_{v_r} = \frac{1/Z_c}{T_r}\left(\frac{\partial (C_v/R)}{\partial v_r}\right)_{T_r} \tag{3-73}$$

from this consistency, it may be concluded that

$$\left(\frac{\partial^2 P_r}{\partial T_r^2}\right)_{v_r} \begin{cases} < 0 & \text{for } v_r > 1 \\ = 0 & \text{for } v_r = 1 \\ > 0 & \text{for } v_{rx} < v_r < 1 \\ = 0 & \text{for } v_r = v_{rx} \\ < 0 & \text{for } v_r < v_{rx} \end{cases} \tag{3-74}$$

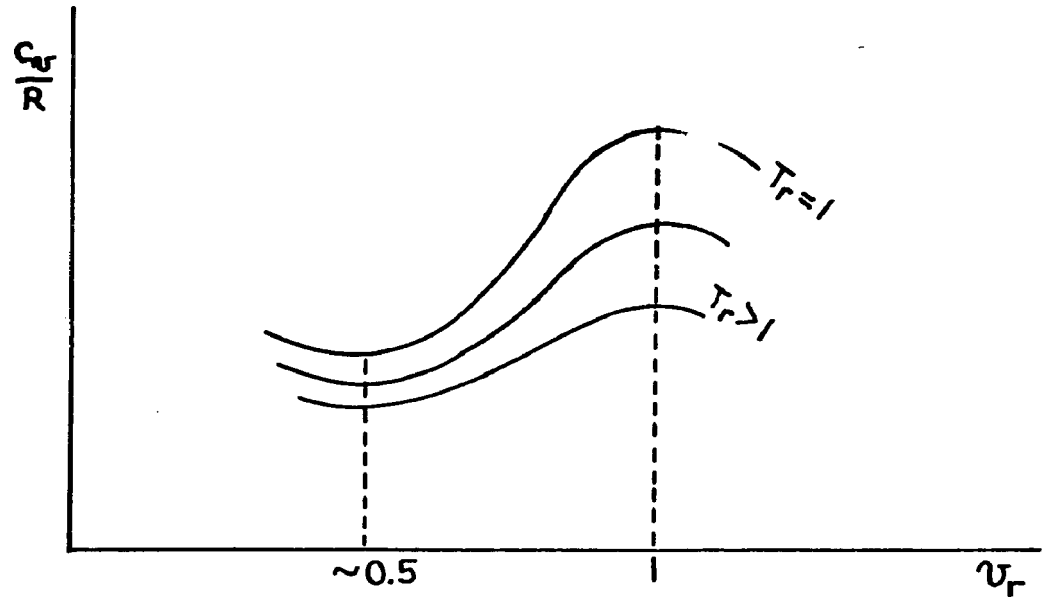


Figure 8. The constant volume specific heat-reduced specific volume plot

where v_{rx} is between about 1/2.0 and 1/1.8. As the temperature increases, the value of the curvatures approaches zero; then, at about more than 2.5 or 3 times critical temperature the curvature becomes negative (Figure 9).

It is also possible to observe directly the thermal-pressure coefficients which are fairly horizontal at the temperatures higher than the critical and then decrease very slowly at high temperatures. At low temperature (less than critical), the thermal-pressure coefficient changes consistently to the behavior of the curvature of the isometrics. Then, it may be concluded that

$$\left(\frac{\partial^2 P_r}{\partial T_r^2}\right) \begin{cases} = 0 & \text{for } 1 < T_r < T_{rx} \\ < 0 & \text{for } T_{rx} < T_r \end{cases} \qquad (3\text{-}75)$$

where T_{rx} is between about 2.5 and 3.

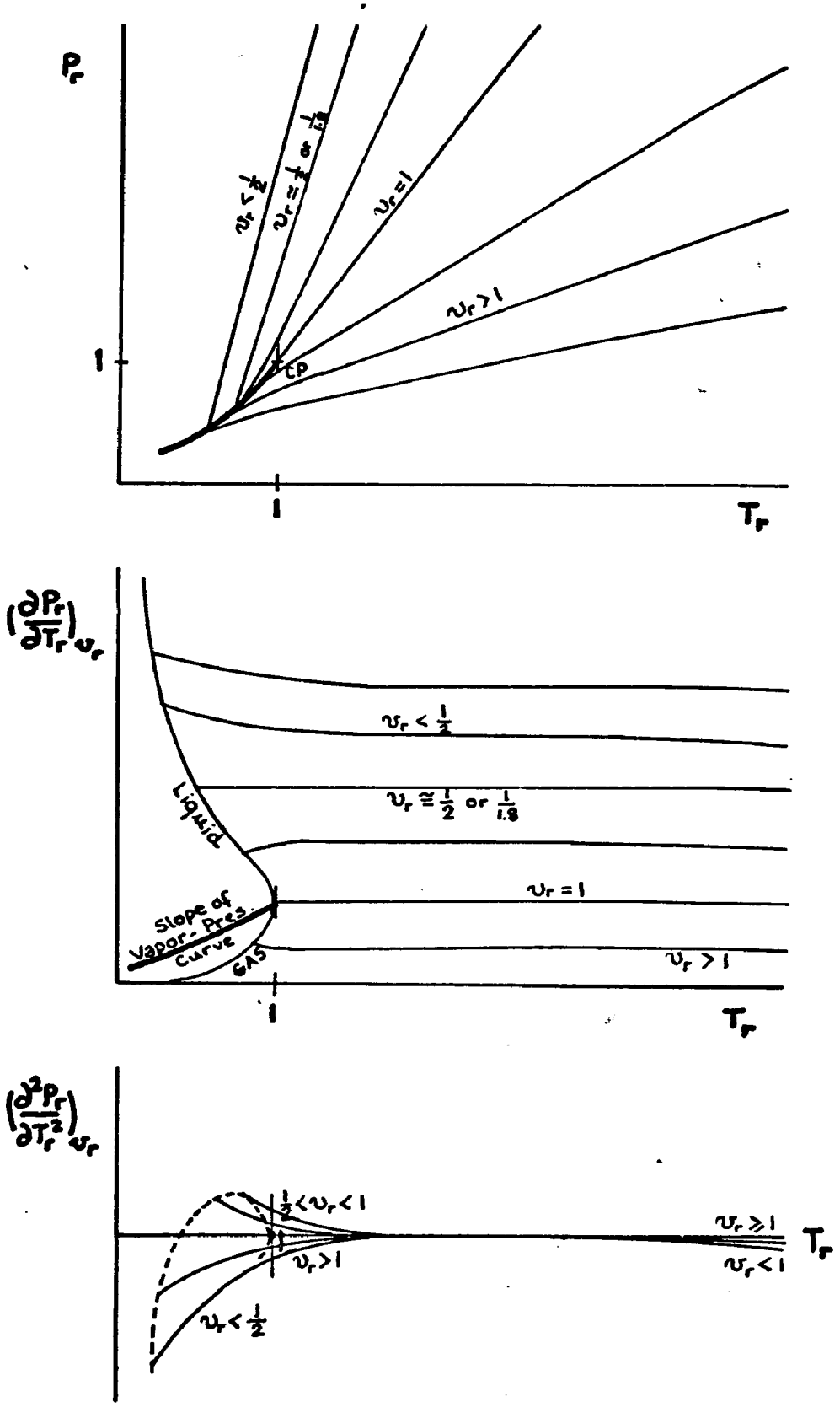


Figure 9. The nature of isometrics: their slopes (thermal-pressure coefficient) and curvatures

It should be noted also that the thermal pressure coefficient at the critical point (the slope of the critical isometrics) is equal to the slope of the vapor-pressure curve.

$$\left(\frac{\partial P_r}{\partial T_r}\right)_{\substack{v_r=1 \\ \text{at } T_r=1}} = \left(\frac{dP_{rsat}}{dT_r}\right)_{\text{at C.P.}} \tag{3-76}$$

However, it is evident (Figure 9) that the curvatures of the critical isometrics and the vapor-pressure curve are not equal. Although the first one is zero, the other is clearly positive.

$$\left(\frac{\partial^2 P_r}{\partial T_r^2}\right)_{\substack{v_r=1 \\ \text{at } T_r=1}} = 0, \qquad \left(\frac{d^2 P_{rsat}}{dT_r^2}\right)_{\text{at C.P.}} > 0 \tag{3-77}$$

Consequently, from the behavior of the curvature of the isometrics and of the thermal-pressure coefficient, it may be stated that the isometrics near the saturated region are concave down below the critical density, then they curve up between the critical density and about 1.8 or 2 times critical density and they are concave down again. The critical isometric and the isometrics in the temperature range between the critical and 2.5 or 3 times critical and for the large specific volumes are straight lines. For the higher densities, the isometrics, at higher temperatures than about 2.5-3 times the critical, are concave down also.

In this work it was observed that mixtures at moderate density are almost straight lines in the temperature range between 100 and 140 K. However, as a matter of fact, they have a negative curvature. Table XII gives the thermal pressure coefficients of the neon-nitrogen system (51.4% of Neon; 48.6% Nitrogen) for two isometrics.

TABLE XII

THE THERMAL PRESSURE COEFFICIENT

OF THE NEON-NITROGEN MIXTURE

T	$(\frac{\Delta P}{\Delta T})_v$	$\frac{atm.}{K}$
K	v=211 $\frac{cc}{mole}$	v=403 $\frac{cc}{mole}$
105		0.233
115	0.484	0.229
125	0.475	0.226
135	0.467	0.224

5. Corresponding States Theory and Generalized Charts. The concept of the corresponding states generates from the characteristic similarity of the PvT behavior of the pure fluids with respect to their critical points. The simplest form of the corresponding states is based on the assumption that the reduced pressure ($P_r=P/P_c$), the reduced volume ($v_r=v/v_c$), the reduced temperature ($T_r=T/T_c$) surface is the same for all substances, which may be formulated as follows:

$$\phi(P_r, v_r, T_r) = 0 \qquad \text{(for all pure fluids)} \tag{3-77}$$

This form, though rough, is a very simple and useful approximation to predict the real behavior of substances.

Generalized charts (either the reduced pressure-reduced volume chart or the compressibility-reduced pressure chart or others) are the representation of the corresponding states theory with two-parameters, such as $P_r=P_r(v_r, T_r)$, $P_r=P_r(v_r', T_r)$, etc.

One of the most common generalized charts is the compressibility-reduced pressure chart. Several generalized compressibility charts are available in the literature (30,45,76); however, the recent charts which are based on a large amount of experimental PvT data of different gases are considered to be the best charts, such as Nelson-Obert (67), Viswanath-Su (102). The comparison of these two compressibility charts in the reduced temperature range from 1.0 to 15.0 and the reduced pressure up to 40.0 indicates that the latter chart is more reasonable than the former.

However, the failure of the two-parameter corresponding states theory, especially near the critical point, led investigators to use a third parameter in order to be able to have a better correlation. The three-parameter corresponding states correlation was thoroughly discussed by Reid and Sherwood (76). Any of the following may be used as a third parameter of the corresponding states: the critical compressibility, Z_c, the acentric factor which is defined as (70),

$$\omega = -1.000 - \log P_{r_{sat}} \quad (T_r=0.7) \tag{3-78}$$

or the Riedel factor which is defined as (78),

$$\alpha_c = \left(\frac{d(\ln P_{r_{sat}})}{d(\ln T_r)}\right)_{T_r=1} = \left(\frac{dP_{r_{sat}}}{dT_r}\right)_{T_r=1} \tag{3-79}$$

As shown in the above equation, α_c is also the slope of the critical isometric. However, α_c is usually calculated from the generalized vapor-pressure equation developed by Riedel. The correspondence between Z_c, ω and α_c may be found in the literature as follows (43,76):

$$Z_c = 0.291 - 0.080\ \omega \tag{3-80}$$

$$\omega = 0.203\ (\alpha_c - 7.00) + 0.242 \tag{3-81}$$

and $$\frac{1}{Z_c} = 3.72 + 0.26\ (\alpha_c - 7.00) \tag{3-82}$$

The acentric factor correlation is more commonly utilized than the others. The convenient expression to determine the compressibility is given as,

$$Z(T_r,P_r) = Z^0(T_r,P_r) + \omega Z^1(T_r,P_r) \qquad (3\text{-}83)$$

where Z^0 is the compressibility factor of the simple fluids represented by argon, krypton, xenon and methane and Z^1 is the compressibility factor correction for the deviation from simple fluids.

Under the same circumstances, Thodos and his co-workers (17,41) developed the generalized reduced density-reduced temperature charts which depend on the critical compressibility for monatomic and diatomic gases. It is concluded that the PvT behavior of substances having approximately the same critical compressibility (i.e. 0.291) shows similar characteristics whether or not the substances are monatomic or diatomic unless the polarity effect is not present (17). Because of the excessive quantum effect on helium, different charts were developed for neon and helium even though their critical compressibilities are very close (41).

Three-parameter corresponding states for nonpolar molecules (neglecting polarity and quantum effects) such as argon, krypton, nitrogen, carbon-monoxide, etc., whose critical compressibilities are almost the same, 0.291, may be preduced easily by applying dimensional analysis to the important system parameters, as follows,

$$\phi_1(P,v,T,P_c,v_c,T_c,R)=0 \qquad \text{(for nonpolar molecules)} \qquad (3\text{-}84)$$

With the convenient arrangement of the dimensionless groups, the expression,

$$\phi_2(P_r,v_r,T_r,Z_r)=0 \qquad \text{(for nonpolar molecules)} \qquad (3\text{-}85)$$

or

$$\phi_3(Z,v_r,T_r,Z_c)=0 \qquad \text{(for nonpolar molecules)} \qquad (3\text{-}86)$$

may be correlated. The additional shape parameter may be required. Thus, four-parameter corresponding states correlation may be derived for non-polar molecules. Martin and Hou (59) proposed the use of the slope of the critical isometric, $\gamma_{V_{r=1}}$, as a fourth parameter. Hirschfelder et al (43) included the Reidel factor, α_c, which is the slope of the vapor-pressure curve at the critical point and is equal to $\gamma_{V_{r=1}}$, as a fourth parameter. Although the relation, equation (3-82), is given between α_c and Z_c, some substances do not obey that relation and therefore Z_c and α_c may be used independently.

Then, including the polarity and quantum effects, the theorem of the corresponding states may be extended and therefore may be more applicable to many substances. Stiel (92) summarized thoroughly the extension of the corresponding states theory. At the present, the corresponding states correlations are used exclusively for the prediction of the thermodynamic properties.

The concept of corresponding states may also be applicable to mixtures, although the PvT behavior of mixtures around the true critical point is evidently different than the pure components behavior. However, considering the empirical pseudo-critical constants concept, extending the corresponding states theory to mixtures becomes possible. This method has been reviewed by several authors (75,76,92). Also, the statistical mechanical approach which has been used by several investigators may be considered for the extension of the corresponding state theory to mixtures.

The other attempt to correlate the mixture properties by means of the corresponding state theory is to determine the interaction second and third virial coefficients. It is assumed that the plots of the re-

duced second virial coefficients for all substances against the reduced temperature are the same curve which may be represented by an equation as follows,

$$B_r = \theta_2(T_r) \qquad \text{(for all substances)} \tag{3-87}$$

where $B_r=B/v_c$, $T_r=T/T_c$. Guggenheim and McGlasham (38) considered that the reduced interaction second virial coefficient would be represented with the same equation (3-87) as,

$$\frac{B_{ij}}{v_{c_{ij}}} = \theta_2 \left(\frac{T}{T_{c_{ij}}}\right) \tag{3-88}$$

where $v_{c_{ij}}$, $T_{c_{ij}}$ are the interaction pseudo-critical constants. Substituting B_{ii}, B_{jj} and B_{ij} which are derived from the equations (3-87) and (3-88) into the following equation (theoretical combining rule for the second virial coefficient)

$$B_m = \sum_i \sum_j y_i y_j B_{ij} \tag{3-89}$$

Then, the equation

$$B_m = \sum_i \sum_j y_i y_j v_{c_{ij}} \theta_2 \left(\frac{T}{T_{c_{ij}}}\right) \tag{3-90}$$

is written. (This expression is related with the two-parameter corresponding states theory).

Later, Prausnitz and Gunn (71) extended the three-parameter corresponding states theory to the interaction second virial coefficient as follows,

$$\frac{B_{ij}}{v_{c_{ij}}} = \theta_2^o \left(\frac{T}{T_{c_{ij}}}\right) + \omega_{ij}\, \theta_2^1 \left(\frac{T}{T_{c_{ij}}}\right) \tag{3-91}$$

where ω_{ij} is the interaction acentric factor (the third parameter), $\theta_2^o (T_r)$ is the expression representing the reduced second virial coeffi-

cient for the simple fluids, $\Theta_2^1(T_r)$ is the correction function for the deviation from the simple fluids. Thus the equation (3-89) may be written

$$B_m = \sum_i \sum_j y_i y_j v_{c_{ij}} \left[\Theta_2^o \left(\frac{T}{T_{c_{ij}}}\right) + \omega_{ij} \; \Theta_2^1 \left(\frac{T}{T_{c_{ij}}}\right)\right] \qquad (3\text{-}92)$$

From this viewpoint, considering the expressions $\Theta_{2i}(T_r)$ and $\Theta_{2j}(T_r)$ (in the same form but with different constants), for the reduced second virial coefficients of pure components i and j, respectively, a new combining rule for the second virial coefficient of the mixture of these two components may be derived.

$$B_{rm}(T_r) = y_i \; \Theta_{2i}(T_r) + y_j \; \Theta_{2j}(T_r) \qquad (3\text{-}93)$$

where $T_r = T/T_{c_m} = T_i/T_{c_i} = T_j/T_{c_j}$ and T_i, T_j represent different temperatures. Those two curves on the B_r vs. T_r plot are almost coincident (Figure 10). Therefore, the most probable argument that can be considered for the second virial coefficient of the mixture is that the curve representing the mixture lies between the former curves. Assuming that the second virial coefficient of the mixture changes linearly with the composition between the two second virial coefficients of pure components at a constant reduced temperature, the above equation (3-93) can be written. Then, equation (3-93) may be written for mixtures having more than two components, as follows,

$$B_{rm}(T_r) = \sum_i^N y_i \; \Theta_{2i}(T_r) \qquad (3\text{-}94a)$$

Under the same consideration, for the reduced third, fourth, etc. virial coefficients for the mixtures the following simple equations may be written,

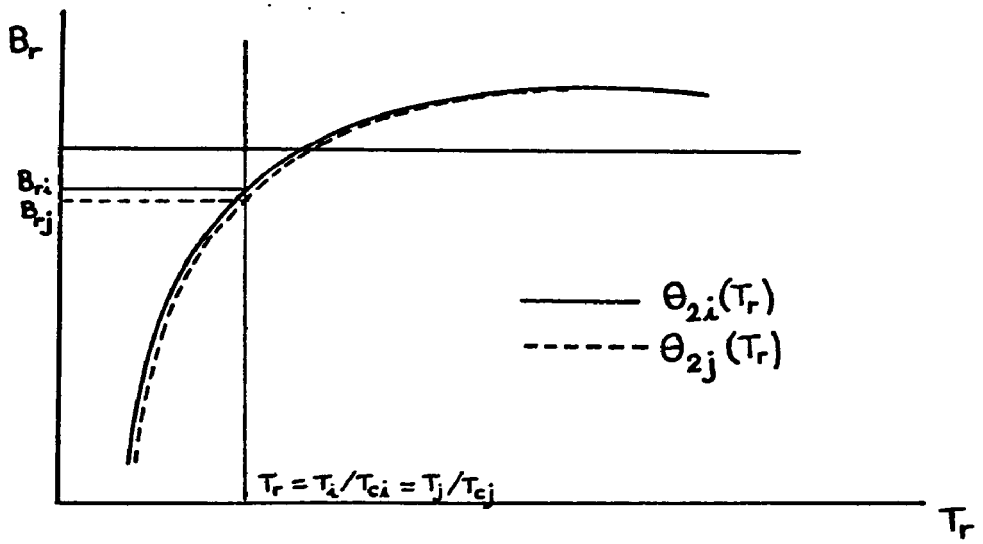


Figure 10. The reduced second virial coefficients of pure components i and j.

$$C_{rm}(T_r) = \sum_{j}^{N} y_i \cdot \Theta_{3i}(T_r) \qquad (3\text{-}94b)$$

$$D_{rm}(T_r) = \sum_{i}^{N} y_i \cdot \Theta_{4i}(T_r) \qquad (3\text{-}94c)$$

etc. If the equations (3-94a), (3-94b), and so forth are substituted into the equation of state in virial form by rearranging the equation,

$$Z_m(T_r,v_r) = 1 + \frac{\sum_{i}^{N} y_i\ \Theta_{2i}(T_r)}{v_r} + \frac{\sum_{i}^{N} y_i\ \Theta_{3i}(T_r)}{v_r^2} + \cdots\cdots$$

$$= \sum_{i=1}^{N} y_i\left(1 + \frac{\Theta_{2i}(T_r)}{v_r} + \frac{\Theta_{3i}(T_r)}{v_r^{\,2}} + \cdots\right) \qquad (3\text{-}95)$$

$$= \sum_{i=1}^{N} y_i Z_i(T_r,v_r)$$

is derived. The assumption of the linear correlation of the mixture virial coefficients from the pure component virial coefficients at a constant reduced temperature implies that the compressibility of the mixture at a given reduced temperature and reduced specific volume may

be determined from linear interpolation of the compressibilities of the pure components, which is in agreement with the generalized compressibility chart. As mentioned above, the generalized compressibility chart representing two-parameter corresponding state theory implies that all gases, including mixtures, have the same compressibility factor at a given reduced temperature and reduced volume (or pressure), although there is a slight difference between the compressibilities of any two pure fluids. Therefore, to correct this slight difference, the linear combination of the compressibilities of the pure fluids, as given in equation (3-95), may be considered to be the mixture compressibility as illustrated in Figure (11).

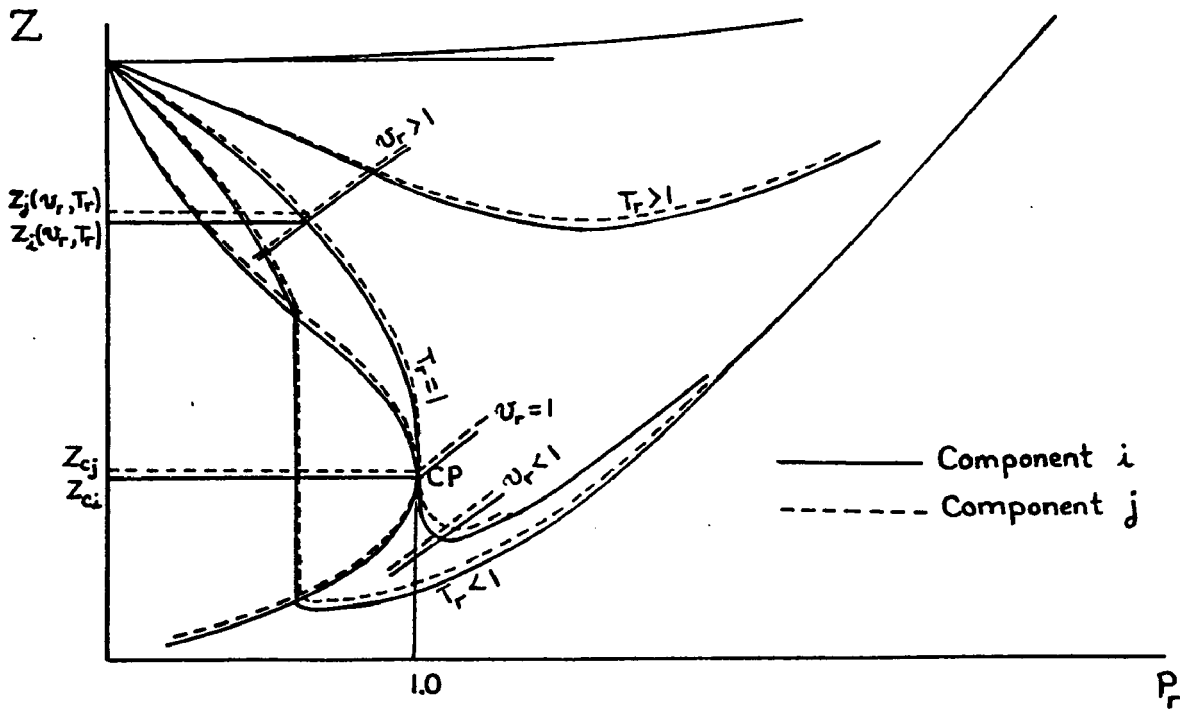


Figure 11. Generalized compressibility chart for two different substances.

6. Pseudo-Critical Constants. The reduced properties of mixtures may be estimated by means of the theorem of corresponding states. Use of the true critical constants of mixtures (mentioned in part B) does not give satisfactory results. Therefore, it is necessary to find another technique so that the mixture properties might be determined accurately. The mixture constants that correspond with the critical constants of the pure components are called "pseudo-critical constants" for mixtures. The pseudo-critical constants of a mixture are completely different, in a physical sense, than the true critical constants.

The pseudo-critical constants are usually determined by means of the combining rules (mentioned in part A.2). The simplest combining rule, Kay's rule, is that the pseudo-critical temperature and pressure are determined by the linear combining rule - equation (3-12). There are several other combining rules for pseudo-critical constants which produce more accurate results for predicting the mixture PvT properties, but they are more complex than Kay's rule. Several authors have discussed and summarized some of those rules (45,76,92).

In general, it is necessary to have sufficient combining rules only for three of the four pseudo-critical constants (P_{cm}, v_{cm}, Z_{cm}, and T_{cm}). The fourth one may be determined from the equation $P_{cm}v_{cm}=Z_{cm}RT_{cm}$.

As simpler combining rules, several investigators adopted the linear combining rule for the pseudo-critical compressibility (20,49,71), volume (39,71) and temperature (71,92), as follows,

$$Z_{cm} = \sum_{i}^{N} y_i Z_{ci} \tag{3-96a}$$

$$v_{cm} = \sum_{i}^{N} y_i v_{ci} \tag{3-96b}$$

$$T_{cm} = \sum_{i}^{N} y_i T_{ci} \tag{3-96c}$$

Besides these, it is common to use the Lorentz combining rule (equation 3-16) for the volume (20,38) and the linear square-root combining rule (equation 3-13) for the temperature (38,84), as follows,

$$v_{cm} = \sum_{i}^{N} \sum_{j}^{N} y_i y_j \left(\frac{v_{ci}^{1/3} + v_{cj}^{1/3}}{2}\right)^3 \tag{3-97a}$$

$$T_{cm} = \left(\sum_{i}^{N} y_i T_{ci}^{1/2}\right)^2 \tag{3-97b}$$

CHAPTER IV

DETERMINATION OF THE CONSTANTS OF THE EQUATION OF STATE

A. GENERAL

While the form of the equation of state was being chosen, the first consideration was to be able to determine the constants of the equation from the general behavior of pure substances. Thus, the corresponding constants for different substances would have the same physical meaning; this would allow the evaluation of the constants for mixtures by using suitable combining rules, which would themselves have a physical meaning. The second consideration was to be able to predict the thermodynamic properties of the pure substances and mixtures more accurately than the other equations, especially in the critical region. For those considerations, Martin's recent equation (1967) (equation 3-25) was indeed satisfactory. During the evaluation of the constants for argon, neon, and nitrogen, some modifications were necessary, and finally the modified equation (3-33) provided a satisfactory representation of the PvT behavior.

Although the constants would be determined by means of the general behavior of substances, because of the inaccuracies of the parameters representing the certain general behavior and also because of the sensitivity of the equation, it was not possible to directly correlate the constants of the equation of state from the analytical relations that will be mentioned in this chapter. Therefore, the method of successive approach was used to evaluate the constants of the pure components.

Perhaps additional work with the numbers and with the analytical relations was required to get the desired accuracy. Nevertheless, the process was useful in understanding the character of the equation of state and the effect of the parameters. Actually, the expression (as well as the equation of state) borrowed from Martin may explain the unexpected aspect of the equation of state: "Because of the apparent simplicity of the task, it is not surprising that many have rushed in where more experienced workers have feared to tread." (46)

B. CONSTANTS FOR PURE COMPONENTS

1. Critical Isotherm. Most equations of state fail in the critical region; therefore, it may be considered that to first fit the equation to the critical isotherm gives a better correlation in the critical region. After rewriting equation (3-34)

$$P_r(T_r,v_r) = \sum_{i=1}^{7} \frac{\tau_i(T_r)}{\Phi_i(v_r)} \qquad (3\text{-}34)$$

where $P_r=P/P_c$, $v_r=v/v_c$, $T_r=T/T_c$ and

$$\tau_i(T_r)=A_{ri} + B_{ri}T_r + C_{ri}\, e^{-k(T_r-1)} \qquad (3\text{-}34a)$$

$$\Phi_i(v_r) = \begin{cases} v_r^i & i=1,\ldots,5 \\ e^{\alpha_{ri}(v_r-1)} & i=6,7 \end{cases} \qquad (3\text{-}34b)$$

$$A_{r1} = C_{r1} = 0, \qquad B_{r1} = 1/Z_c$$

The equation may be written for the critical isotherm ($T_r=1$) as follows,

$$P_r(1,v_r) = P_{r1}(v_r) = \sum_{i=1}^{7} \frac{\tau_{i1}}{\Phi_i(v_r)} \qquad (4\text{-}1)$$

where,

$$\tau_{11} = 1/Z_c$$

$$\tau_{i1} = \tau_i(1) = A_{ri} + B_{ri} + C_{ri} \qquad i=2,\ldots,7 \tag{4-1a}$$

are constants, $\Phi_i(v_r)$ are the same as in equation (3-34b). There are eight unknowns: $\tau_{21}, \tau_{31}, \tau_{41}, \tau_{51}, \tau_{61}, \tau_{71}, \alpha_{r6}$, and α_{r7}; but only three relations, as

$$P_r(1,1) = 1 \tag{4-2}$$

$$\left(\frac{\partial P_r}{\partial v_r}\right)_{T_r=1 \text{ at } v_r=1} = 0 \tag{3-36}$$

$$\left(\frac{\partial^2 P_r}{\partial v_r^2}\right)_{T_r=1 \text{ at } v_r=1} = 0 \tag{3-37}$$

As mentioned previously (Chapter III, part B.1), the third and fourth derivatives at the critical point might not be assumed to be zero. If it is desirable to use the relations,

$$\left(\frac{\partial^3 P_r}{\partial v_r^3}\right)_{T_r=1 \text{ at } v_r=1} = -\varepsilon_3 \tag{3-38}$$

$$\left(\frac{\partial^4 P_r}{\partial v_r^4}\right)_{T_r=1 \text{ at } v_r=1} = \varepsilon_4 \tag{3-39}$$

two more unknowns (ε_3, ε_4) will be added. By the application of equation (4-1) to the relations (4-2) and (3-36) through (3-39) the following results are produced, respectively:

$$P_r(1,1) = \sum_{i=1}^{7} \tau_{i1} = 1 \tag{4-3}$$

$$\left(\frac{\partial P_r}{\partial v_r}\right)_{\substack{T_r=1 \\ \text{at } v_r=1}} = -\sum_{i=1}^{5} i\tau_{i1} - \sum_{i=6}^{7} \alpha_{ri} \tau_{i1} = 0 \tag{4-4}$$

$$\left(\frac{\partial^2 P_r}{\partial v_r^2}\right)_{\substack{T_r=1 \\ \text{at } v_r=1}} = \sum_{i=1}^{5} i(i+1) \tau_{i1} + \sum_{i=6}^{7} \alpha_{ri}^2 \tau_{i1} = 0 \tag{4-5}$$

$$\left(\frac{\partial^3 P_r}{\partial v_r^3}\right)_{\substack{T_r=1 \\ \text{at } v_r=1}} = -\sum_{i=1}^{5} i(i+1)(i+2) \tau_{i1} - \sum_{i=6}^{7} \alpha_{ri}^3 \tau_{i1} = -\varepsilon_3 \tag{4-6}$$

$$\left(\frac{\partial^4 P_r}{\partial v_r^4}\right)_{\substack{T_r=1 \\ \text{at } v_r=1}} = \sum_{i=1}^{5} i(i+1)(i+2)(i+3) \tau_{i1} + \sum_{i=6}^{7} \alpha_{ri}^4 \tau_{i1} = \varepsilon_4 \tag{4-7}$$

Consequently, two different equation sets [(i) equations (4-3) through (4-5); (ii) equations (4-3) through (4-7)] are regarded as being able to determine the constants of the critical isotherm. Both sets need five more relations or the experimental PvT data with a high accuracy for the critical isotherm (Table III-1,2,3) in order to determine the constants completely. The equation sets may be referred to as "τ-equation set" and "ε-equation set" according to whether or not it includes ε_3, ε_4. In the τ-equation set, τ_{21}, τ_{31}, τ_{41}, α_{r6} and the ratio of the α_{r7} to α_{r6} ($m = \alpha_{r7}/\alpha_{r6}$) and in the ε-equation set, τ_{21}, ε_3, ε_4, α_{r6}, and m were chosen as parameters; then the other constants were determined in this work. The preliminary values of some of those parameters were obtained from the theorem of corresponding states. τ_{21},

τ_{31},..... are related to the reduced second, third, and so forth, virial coefficients as -- from equations (3-55), (3-71), (3-72)....--

$$\tau_{21} = B_r(1)/Z_c = \beta_1/Z_c^2 \qquad (4\text{-}8a)$$

$$\tau_{31} = C_r(1)/Z_c = \gamma_1/Z_c^3 \qquad (4\text{-}8b)$$

. . . . . .

respectively. Here, B_r, C_r, ... are the reduced second, third, ... virial coefficients, $\beta_1 = B(T_c)\cdot P_c/RT_c$, $\gamma_1 = C(T_c)\cdot P_c^2/R^2T_c^2$,..., and B, C,... are the second, third,...virial coefficients (Chapter III, part B.2 and 3). Although the values of the second and, perhaps the third virial coefficients are available in the literature ($\beta_1 \approx 1.333$, $\gamma_1 \approx 0.04$), τ_{41}, α_{r6}, and m (for the τ-set) and ε_3, ε_4, α_{r6}, m(for the ε-set) are not known. τ_{41} may be estimated, as a first approximation, from equation (4-3) vanishing τ_{51}, τ_{61}, τ_{71}. Then, α_{r6} and m may be roughly chosen as $\alpha_{r6} \approx 8.00\text{-}10.0$ and m=2.0.

At the beginning of this work, the values of ε_3 and ε_4, except assuming them to be zero, were not known. Perhaps, more work is needed on the third and fourth derivatives for the pure substances in order to generalize the behavior of the critical isotherm by means of ε_3 and ε_4, or vice versa. However, the reduced pressure-reduced specific volume plot (Figure 4) and Table XI may be helpful in estimating the approximate values of ε_3 and ε_4.

Thus, τ_{51}, τ_{61}, τ_{71}, ε_3, and ε_4 are solved as functions of the parameters of τ_{21}, τ_{31}, τ_{41}, α_{r6} and m (from the τ-equation set), or τ_{31}, τ_{41}, τ_{51}, τ_{61} and τ_{71} as functions of the parameters of τ_{21}, ε_3, ε_4, α_{r6} and m (from the ε-equation set). The solutions of the equations may be written as follows:

$$\tau_{i1} = \frac{\Delta_{\tau i}}{\Delta_{\tau}} \qquad i = 6,7 \tag{4-9}$$

where

$$\Delta_{\tau i} = (-1)^i \begin{vmatrix} x_{67} & x_{\tau i} \\ y_{67} & y_{\tau i} \end{vmatrix} \tag{4-9a}$$

$$\Delta_{\tau} = \begin{vmatrix} x_{\tau 6} & x_{\tau 7} \\ y_{\tau 6} & y_{\tau 7} \end{vmatrix} \tag{4-9b}$$

and for the τ-set (τ_{21}, τ_{31}, τ_{41}, α_{r6}, m)

$$\left.\begin{aligned} x_{67} &= -5 + 4\ \tau_{11} + 3\ \tau_{21} + 2\ \tau_{31} + \tau_{41} \\ y_{67} &= 20 - 12\ \tau_{11} - 6\ \tau_{21} - 2\ \tau_{31} \\ x_{\tau i} &= \alpha_{ri} - 5 \\ y_{\tau i} &= \alpha_{ri}^2 - 10\ \alpha_{ri} + 20 \end{aligned}\right\} i = 6,7 \tag{4-10a}$$

for the ε-set (τ_{21}, ε_3, ε_4, α_{r6}, m),

$$\left.\begin{aligned} x_{67} &= \varepsilon_3 - 60 + 24\ \tau_{11} + 6\ \tau_{21} \\ y_{67} &= \varepsilon_4 - 20\ \varepsilon_3 + 120 - 24\ \tau_{11} \\ x_{\tau i} &= \alpha_{ri}^3 - 15\ \alpha_{ri}^2 + 60\ \alpha_{ri} - 60 \\ y_{\tau i} &= \alpha_{ri}^4 - 20\ \alpha_{ri}^3 + 120\ \alpha_{ri}^2 - 240\ \alpha_{ri} + 120 \end{aligned}\right\} i = 6,7 \tag{4-10b}$$

After τ_{61}, τ_{71} are solved, τ_{51} is found by the following equation

$$\tau_{51} = 1 - \tau_{11} - \tau_{21} - \tau_{31} - \tau_{41} - \tau_{61} - \tau_{71} \tag{4-11a}$$

for the τ-set. And τ_{51}, τ_{41}, and τ_{31} are found by the following equations

$$\tau_{51} = 6 - 3\ \tau_{11} - \tau_{21} - \frac{\alpha_{r6}^2 - 8\ \alpha_{r6} + 12}{2} \tau_{61} - \frac{\alpha_{r7}^2 - 8\ \alpha_{r7} + 2}{2} \tau_{71} \tag{4-11b}$$

$$\tau_{41} = -3 + 2\ \tau_{11} + \tau_{21} - 2\ \tau_{51} - (\alpha_{r6} - 3)\ \tau_{61} - (\alpha_{r7} - 3)\ \tau_{71} \tag{4-12}$$

$$\tau_{31} = 1 - \tau_{11} - \tau_{21} - \tau_{41} - \tau_{51} - \tau_{61} - \tau_{71} \tag{4-13}$$

for the ε-set. It should be noted that $\tau_{11} = 1/Z_c$ is calculated from the critical constants (Table II).

After evaluating all of the constants, the equation of the critical isotherm is tested with the experimental data (Table III-1,2,3). The constants used as parameters have different influences in the different density region and for the different equation sets (τ-set or ε-set). Therefore, it is necessary to determine the effect of each parameter for each equation set. These may be done by computing the change of the calculated pressure or compressibility, or the change of the deviation percentage, Δ(Dev. %), as only one of these parameters is changing. Here,

$$\text{Dev. \%} = \frac{P_{cal}-P_{exp}}{P_{exp}} \cdot 100 + \frac{Z_{cal}-Z_{exp}}{Z_{exp}} \cdot 100 \qquad (4\text{-}14)$$

$$\Delta(\text{Dev. \%}) = \frac{P_{cal_2}-P_{cal_1}}{P_{exp}} 100 = \frac{Z_{cal_2}-Z_{cal_1}}{Z_{exp}} 100 \qquad (4\text{-}15)$$

where P_{cal_1}, P_{cal_2} and Z_{cal_1}, Z_{cal_2} are the calculated pressures and compressibilities before and after a parameter changes, respectively.

Figures 12 a through 12 j, which have been plotted with the results for argon, show, as a function of reduced volume, the change of the percentage deviation, Dev. %, when each parameter (α_{r6}, τ_{21}, τ_{31}, τ_{41}, m which were used in the τ-equation set; α_{r6}, τ_{21}, ε_3, ε_4, m which were used in the ε-equation set and Z_c) changes while the remaining parameters are held constant. (+) and (-) signs represent an increase and a decrease, respectively, in the change of Dev. % when a parameter increases (referred to by $\nearrow$) or decreases (referred to by $\searrow$) as a certain given amount shown in the figures. The numerical value of the Δ(Dev. %) may vary according to the different values of the para-

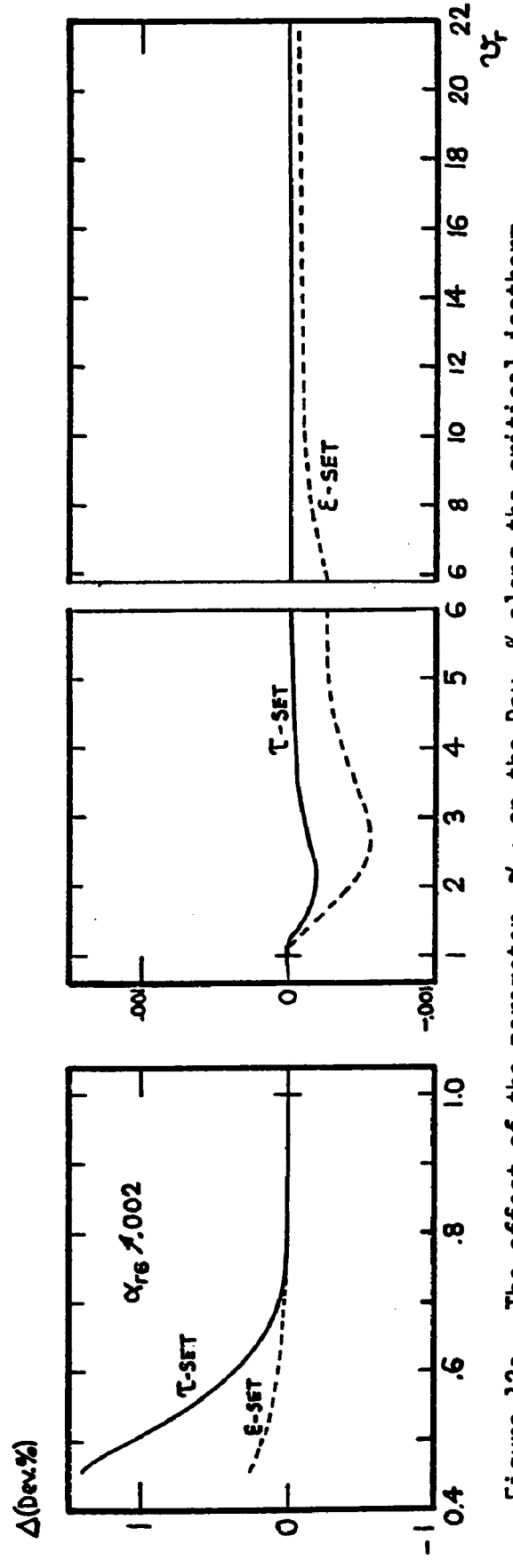


Figure 12a. The effect of the parameter α_{r6} on the Dev. % along the critical isotherm

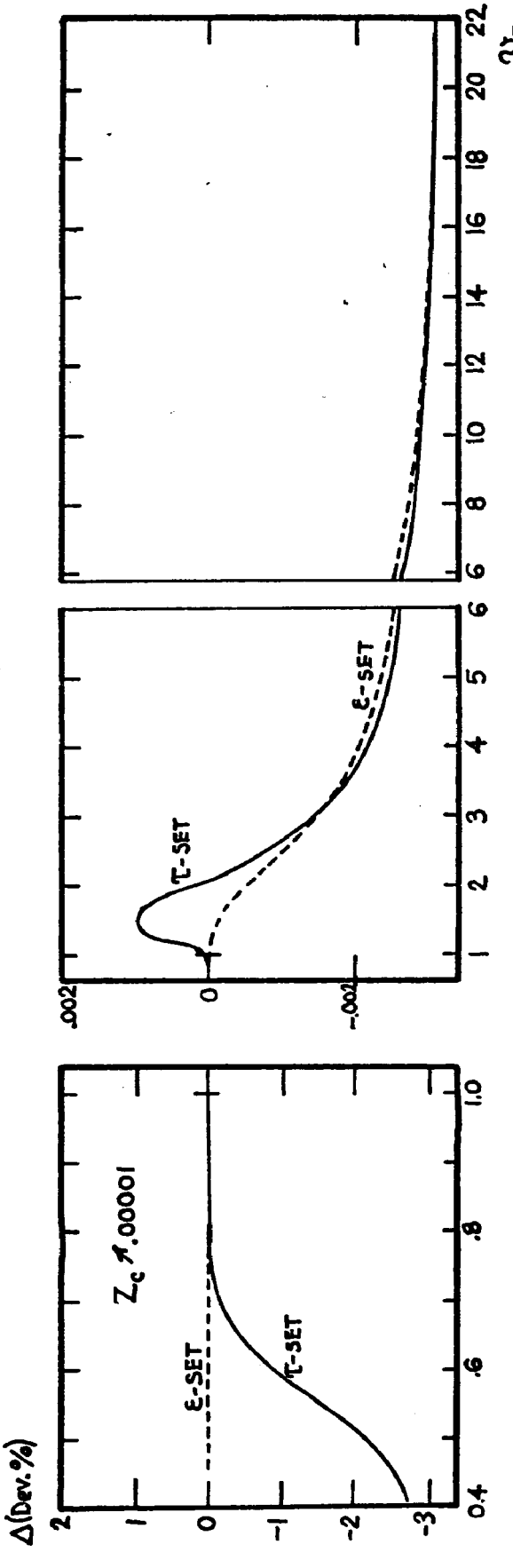


Figure 12b. The effect of Z_c on the Dev. % along the critical isotherm.

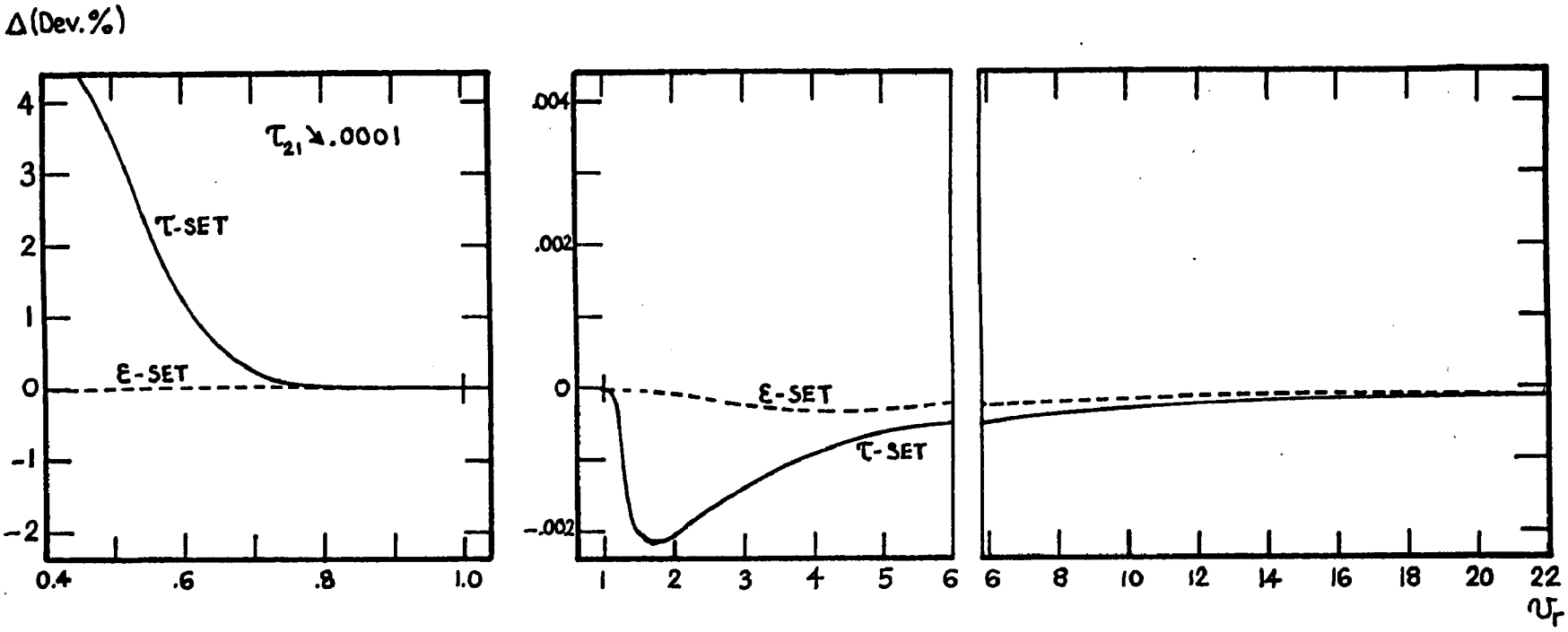


Figure 12c. The effect of the parameter τ_{21} on the Dev. % along the critical isotherm

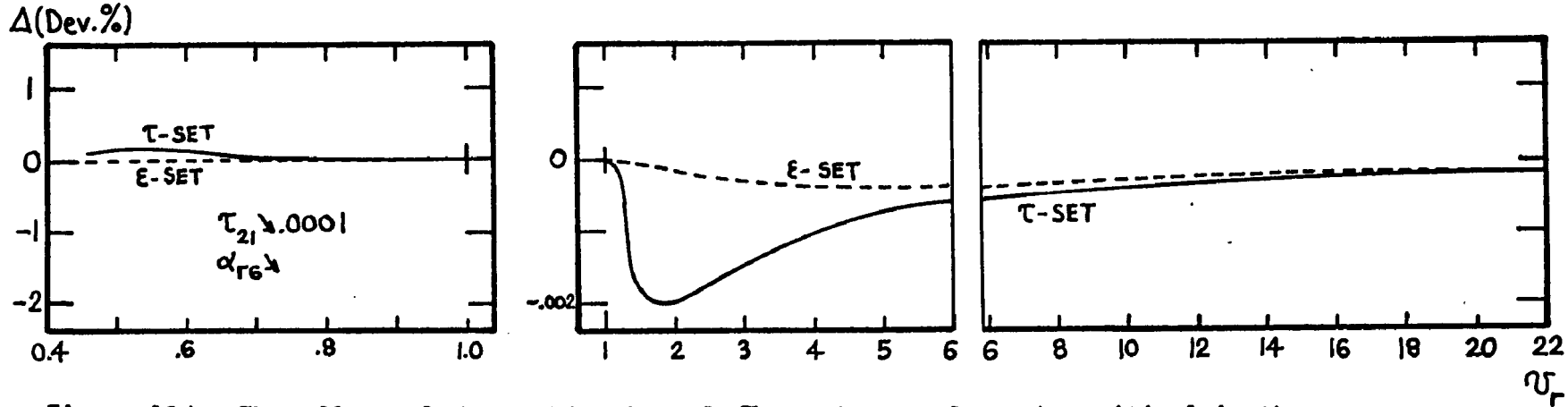


Figure 12d. The effect of the combination of τ_{21} and α_{r6} along the critical isotherm

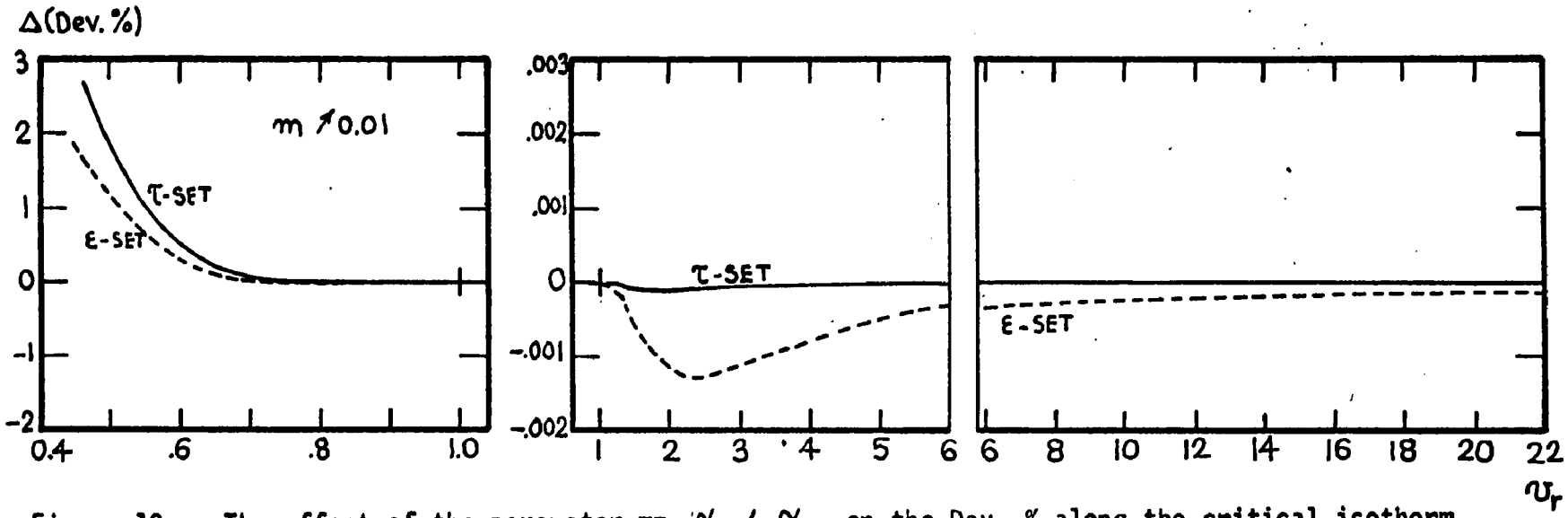


Figure 12e. The effect of the parameter m= $\alpha_{r7}/\ \alpha_{r6}$ on the Dev. % along the critical isotherm

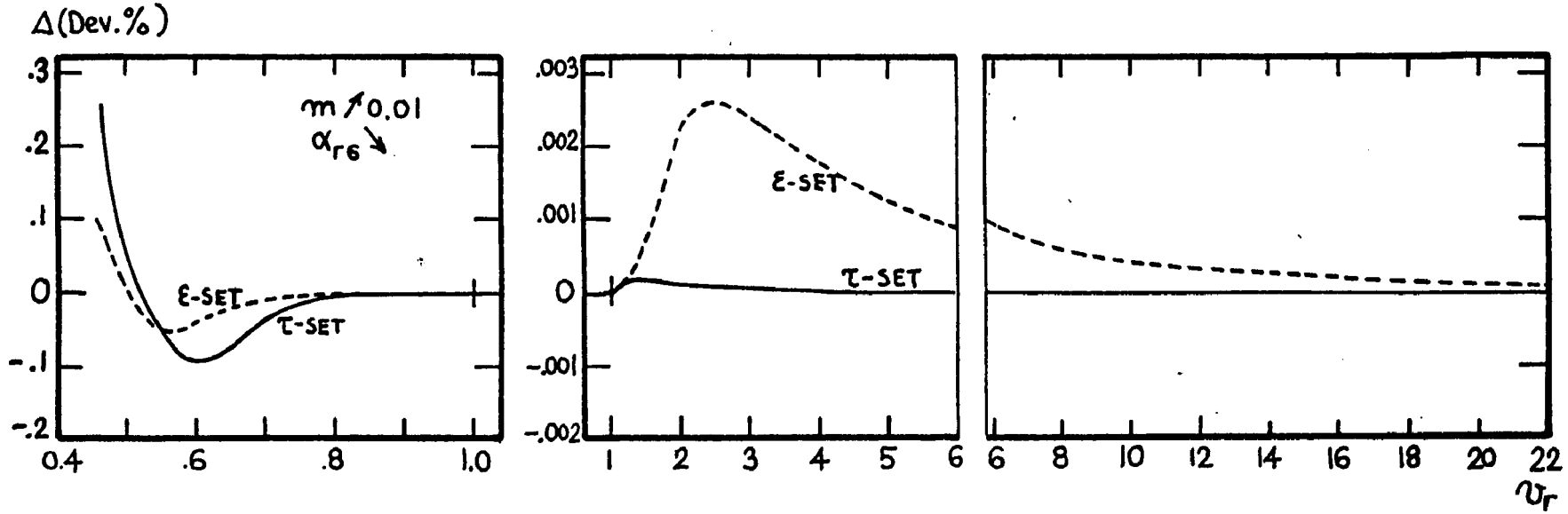


Figure 12f. The effect of the combination of the parameters m and α_{r6} along the critical isotherm

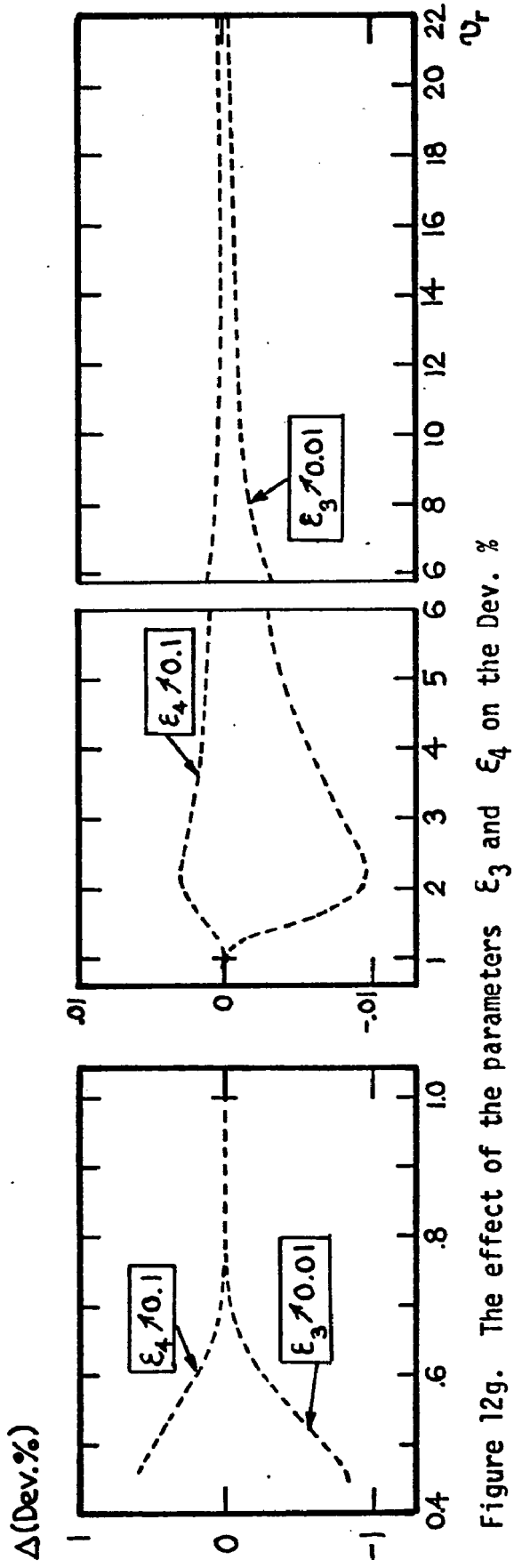


Figure 12g. The effect of the parameters ε_3 and ε_4 on the Dev. %

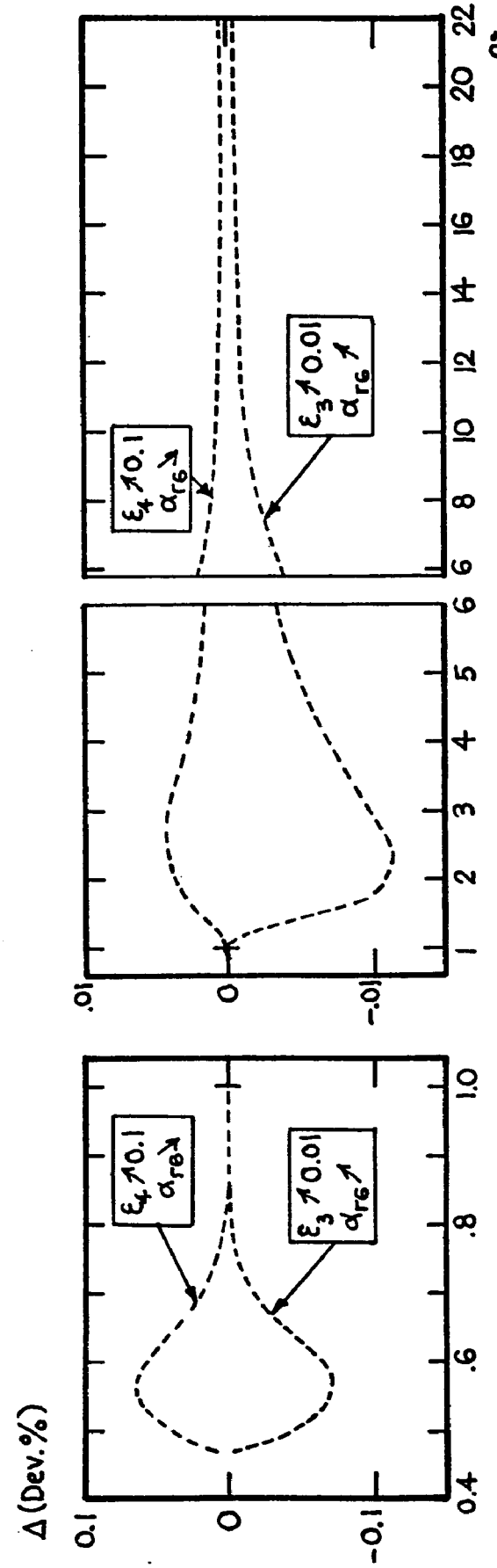


Figure 12h. The effect of the combination of the parameters ε_3 and ε_4 with α_{r6}

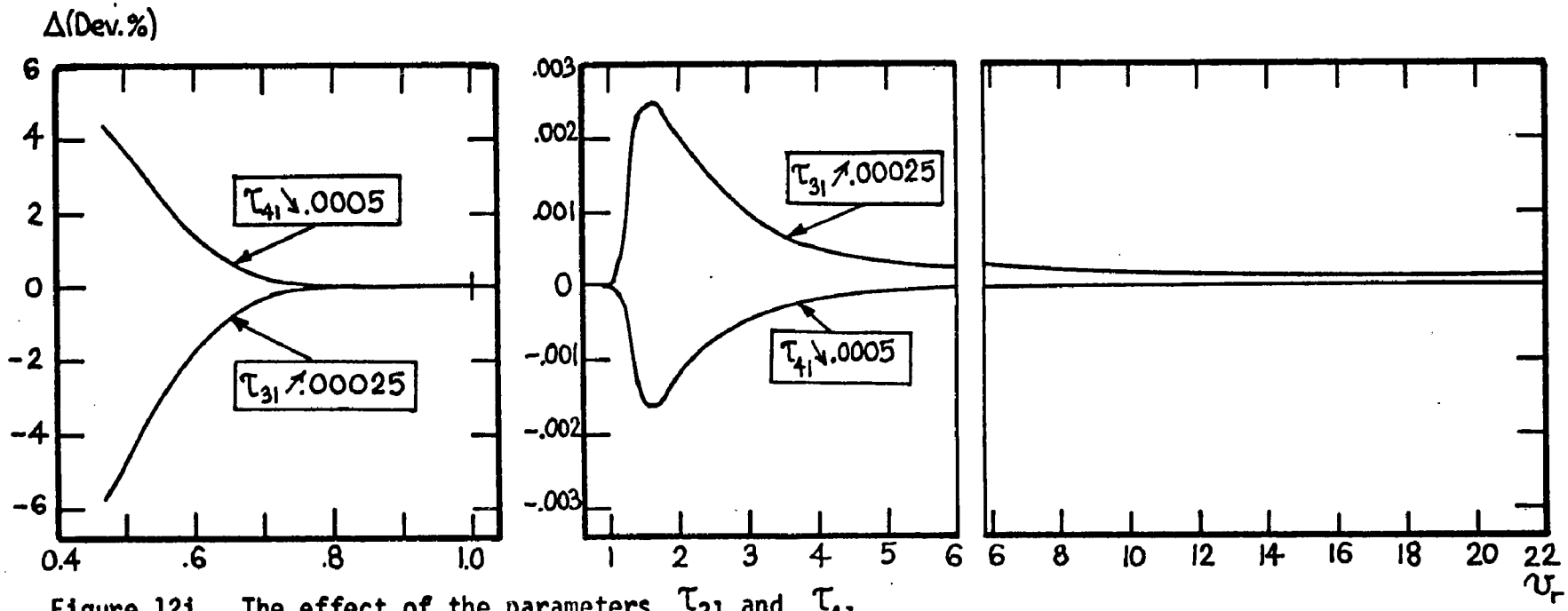


Figure 12i. The effect of the parameters τ_{31} and τ_{41}

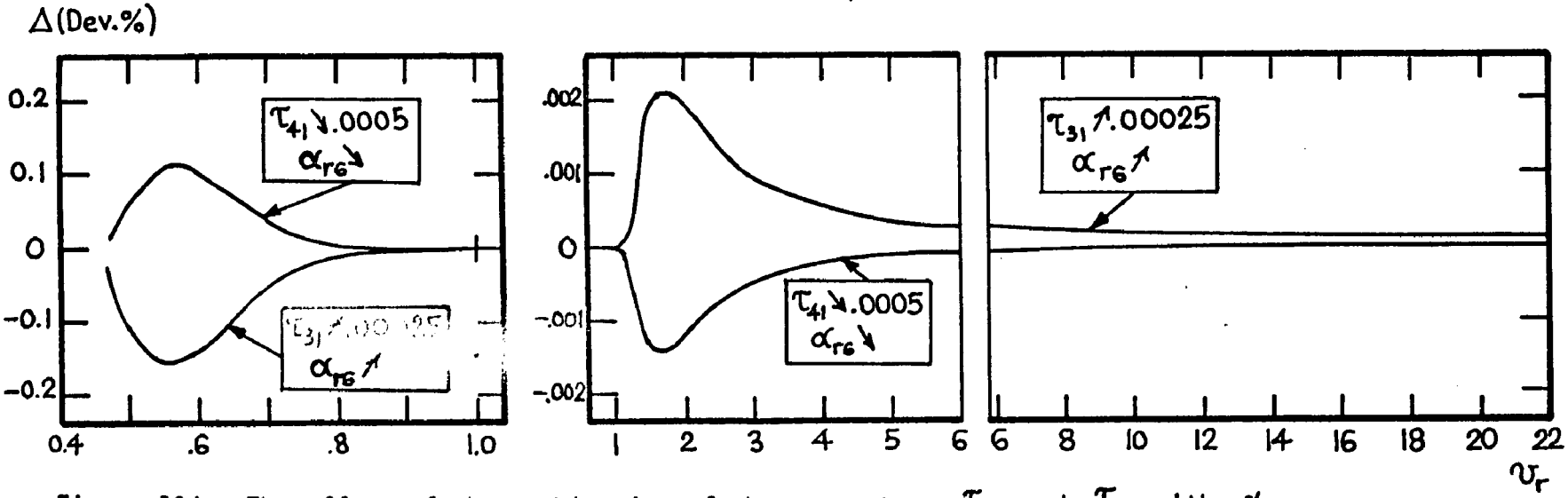


Figure 12j. The effect of the combination of the parameters τ_{31} and τ_{41} with α_{r6}

meters, but the order of magnitude and direction are always the same as shown in the figures. The results for neon and nitrogen are similar.

All of the parameters are highly effective in the high density region and the percentage deviation does not change very much in the low density region (Figures 12a,c,e,g, and i). However, it should be noted that the parameters are changed in very small quantities (0.0001 for τ_{21}, 0.00025 for τ_{31}, 0.0005 for τ_{41}, etc.)

The effect of the α_{r6}, especially in the τ-equation set, was negligibly small in the low density region; therefore, the combinations of the other parameters with α_{r6} were considered in order to eliminate their high effectiveness in the high density region (Figures 12d,f,h, and j). Then, various combinations of these in either the τ-set or the ξ-set were applied successively according to the preceding result of the percentage deviation.

Figures 12b show that a very small change on the critical compressibility effects the percentage deviation considerably more than all of the other parameters in the very low density range. However, in this work, Z_c, was kept constant at the values obtained with the critical constants listed in Table II and with the gas constant R=82.0597 cc-atm/mole K.

The constants for the critical isotherm of argon, neon, and nitrogen, the experimental and calculated pressure compressibility, and the percentage deviation are presented in Table XIII-1,2,3 as computed with the computer.

2. Overall Temperature Range. After the determination of the constants of the critical isotherm, equation (4-1a) gives six constraints among A_{ri}, B_{ri}, and C_{ri}'s:

TABLE XIII-1

ARGON :

TC = 150.860 K
PC = 48.340 ATM.
VC = 74.560 CC/MOLE
ZC =0.291144

T11 = 0.343472E 01
T21 =-0.393676E 01
T31 = 0.147270E 01
T41 =-0.110830E 00
T51 = 0.203571E 00
T61 =-0.638672E-01
T71 = 0.464395E-03

BET1=-0.333700E 00
GAM1= 0.363446E-01
DEL1=-0.796327E-03

ALF6= 0.879000E 01
ALF7= 0.162615E 02

P(1,1)= 1.000
DP(1,1)= 0.000
D2P(1,1)=-0.000
D3P(1,1)=-2.560
D4P(1,1)=40.299

V CC/MOLE	P-EXP. ATM.	P-CAL. ATM.	Z-EXP	Z-CAL	DEV.%
34.916	302.694	302.634	0.854	0.854	-0.017
36.815	211.954	212.316	0.630	0.631	0.171
38.835	150.897	151.063	0.473	0.474	0.110
41.005	110.288	110.291	0.365	0.365	0.002
43.099	86.328	86.206	0.301	0.300	-0.141
46.420	65.533	65.479	0.246	0.246	-0.083
49.108	57.203	57.224	0.227	0.227	0.036
51.822	52.757	52.830	0.221	0.221	0.139
55.002	50.203	50.292	0.223	0.223	0.176
62.167	48.558	48.573	0.244	0.244	0.032
74.560	48.340	48.340	0.291	0.291	-0.000
107.641	47.664	47.634	0.414	0.414	-0.064
126.970	46.359	46.336	0.475	0.475	-0.048
150.924	44.123	44.133	0.538	0.538	0.024
189.509	40.142	40.167	0.615	0.615	0.061
235.640	35.695	35.716	0.679	0.680	0.057
297.371	30.769	30.777	0.739	0.739	0.026
386.536	25.451	25.452	0.795	0.795	0.005
480.811	21.432	21.434	0.832	0.832	0.012
650.902	16.414	16.411	0.876	0.876	-0.022
995.756	11.397	11.395	0.917	0.917	-0.018
1585.804	7.396	7.393	0.947	0.947	-0.045

TABLE XIII-2

__NEON__:

TC = 44.400 K
PC = 26.190 ATM.
VC = 41.744 CC/MOLE
ZC =0.300066

T11 = 0.333260E 01
T21 =-0.361175E 01
T31 = 0.113881E 01
T41 =-0.162608E-01
T51 = 0.219960E 00
T61 =-0.637191E-01
T71 = 0.355911E-03

BET1=-0.325200E 00
GAM1= 0.307681E-01
DEL1=-0.131827E-03

ALF6= 0.888500E 01
ALF7= 0.164372E 02

P(1,1)= 1.000
DP(1,1)= 0.000
D2P(1,1)=-0.000
D3P(1,1)=-2.770
D4P(1,1)=41.299

V CC/MOLE	P-EXP. ATM.	P-CAL. ATM.	Z-EXP	Z-CAL	DEV.%
19.256	180.119	180.218	0.952	0.952	0.055
20.261	129.109	127.780	0.718	0.711	-1.098
21.050	98.227	99.456	0.568	0.575	1.251
22.152	72.420	72.561	0.440	0.441	0.194
24.046	46.853	47.190	0.309	0.311	0.719
24.837	41.739	41.225	0.285	0.281	-1.231
27.178	31.611	31.583	0.236	0.236	0.229
28.303	29.508	29.533	0.229	0.229	0.083
30.851	27.305	27.226	0.231	0.231	-0.289
32.451	26.697	26.662	0.238	0.237	-0.132
33.786	26.584	26.423	0.247	0.245	-0.605
35.811	26.468	26.260	0.260	0.258	-0.787
38.640	26.308	26.197	0.279	0.278	-0.424
39.144	26.305	26.194	0.283	0.281	-0.423
40.079	26.202	26.191	0.288	0.288	-0.043
41.744	26.190	26.190	0.300	0.300	-0.000
66.865	25.371	25.353	0.466	0.465	-0.071
82.637	23.957	23.958	0.543	0.543	0.004
85.894	23.647	23.632	0.557	0.557	-0.061
104.274	21.750	21.743	0.622	0.622	-0.031
107.924	21.324	21.374	0.632	0.633	0.234
163.338	16.651	16.630	0.746	0.746	-0.123
233.609	12.736	12.747	0.817	0.817	0.086
236.595	12.602	12.619	0.818	0.819	0.138
364.935	8.787	8.791	0.880	0.881	0.046
570.050	5.809	5.803	0.[illegible]	0.924	-0.105

TABLE XIII-3

NITROGEN :

TC = 126.200 K
PC = 33.500 ATM.
VC = 90.100 CC/MOLE
ZC =0.291461

T11 = 0.343099E 01
T21 =-0.395529E 01
T31 = 0.167961E 01
T41 =-0.504855E 00
T51 = 0.420449E 00
T61 =-0.712050E-01
T71 = 0.304411E-03

BET1=-0.336000E 00
GAM1= 0.415861E-01
DEL1=-0.364324E-02

ALF6= 0.908300E 01
ALF7= 0.154411E 02

P(1,1)= 1.000
DP(1,1)= 0.000
D2P(1,1)=-0.000
D3P(1,1)=-1.910
D4P(1,1)=27.300

V CC/MOLE	P-EXP. ATM.	P-CAL. ATM.	Z-EXP	Z-CAL	DEV.%
44.971	130.335	130.704	0.566	0.568	0.352
49.701	71.540	71.556	0.343	0.343	0.022
54.895	47.127	46.813	0.250	0.248	-0.666
62.348	36.241	36.256	0.218	0.218	0.041
65.992	34.530	34.719	0.220	0.221	0.548
69.782	33.900	33.997	0.228	0.229	0.287
69.975	33.963	33.974	0.229	0.230	0.035
77.695	33.581	33.557	0.252	0.252	-0.072
81.142	33.510	33.517	0.263	0.263	0.020
90.100	33.500	33.500	0.291	0.291	-0.000
107.853	33.460	33.447	0.348	0.348	-0.038
127.244	33.170	33.127	0.408	0.407	-0.131
130.504	33.080	33.038	0.417	0.416	-0.126
148.984	32.390	32.365	0.466	0.466	-0.076
159.034	31.870	31.897	0.489	0.490	0.086
169.325	31.340	31.364	0.512	0.513	0.078
190.155	30.160	30.182	0.554	0.554	0.072
207.776	29.110	29.132	0.584	0.584	0.074
238.717	27.280	27.296	0.629	0.629	0.058
317.418	23.130	23.152	0.709	0.710	0.097
417.721	19.160	19.162	0.773	0.773	0.008
754.421	11.930	11.930	0.869	0.869	-0.002
1165.912	8.110	8.116	0.913	0.914	0.078
1480.341	6.513	6.517	0.931	0.932	0.065

ALL DATA HAVE BEEN PROCESSED

STOP 0

$$A_{ri} + B_{ri} + C_{ri} = \tau_{i1} \qquad i = 2, \ldots\ldots, 7 \qquad (4\text{-}1a)$$

On the other hand, $B_{ri} = 1/Z_c$, α_{r6} and α_{r7} were determined as mentioned in the previous section. If k = 5.475 was assumed as proposed by Martin (59), twelve more relations would be needed in order to evaluate all of the constants. Those relations were evaluated from several general aspects of behavior of substances, most of them having been suggested by Martin (57).

a) The Second and Third Virial Coefficients. The reduced second and third virial coefficients for the equation of state are given by equations (3-55) and (3-72), respectively. (Chapter III, Part B.2, 3). The relations between the virial coefficients and $\tau_i(T_r)$'s may be written as follows:

$$\tau_2(T_r) = B_r(T_r)/Z_c = \beta(T)/Z_c^2 \qquad (4\text{-}16a)$$

$$\tau_3(T_r) = C_r(T_r)/Z_c = \gamma(T)/Z_c^3 \qquad (4\text{-}16b)$$

where B_r, C_r, ... are the reduced second, third, ... virial coefficients, $\beta(T) = \frac{B(T)\cdot P_c}{RT_c}$, $\gamma(T) = \frac{C(T)\cdot P_c^2}{R^2T_c^2}$, ... and B, C,.... are the second, third,... virial coefficients.

It is well-known that the second virial coefficient becomes zero at the Boyle temperature. The value of the reduced Boyle temperature, T_{Br}, varies between 2.1 and 3.3, but for most substances it is approximately between 2.3 and 2.6. For the third virial coefficient, Martin (57), suggested to read off the value at the Boyle temperature from the generalized third virial coefficient vs. the reduced temperature plot. Thus, the following relations may be written:

$$\tau_i(T_{Br}) = \tau_{iB} = A_{ri} + B_{ri}T_{Br} + C_{ri}e^{-k(T_{Br}-1)} \qquad i=2,3 \qquad (4\text{-}17)$$

where

$$\tau_{2B}=0 \text{ and } \tau_{3B} = C_r(T_{Br})/Z_c = \gamma(T_B)/Z_c^3.$$

Other relations for the second and third virial coefficients were suggested by Martin (57). The slope of one of the reduced isotherms on the Z-P_r plot, in other words, the value of the reduced second virial coefficient B_r' at a reduced temperature, T_r' is equal to Z_c-1. This reduced temperature is about 0.8. Martin and Hou (59) proposed that T_r' is a function of Z_c. The value of the third virial coefficient at this temperature may be read from the generalized third virial coefficient plot. These yield:

$$\tau_i(T_r') = \tau_i' = A_{ri} + B_{ri} T_r' + C_{ri} e^{-k(T_r'-1)} \qquad i=2,3 \qquad (4\text{-}18)$$

where $\tau_2' = -(1-Z_c)\left(\frac{T_r'}{Z_c}\right)^2$ and $\tau_3' = C_r(T_r')/Z_c = \gamma(T')/Z_c^3$. However, another feature of general behavior of the third virial coefficient was used in this work. The third virial coefficient has a maximum value at the reduced temperature, T_r'', approximately between 0.8 - 0.9. From equation (3-72), the following relation may be derived,

$$\frac{dC_r(T_r)}{dT_r} = \frac{A_{r3}Z_c}{T_r''^2} + \frac{C_{r3}Z_c}{T_r''^2}(1 + kT_r'') e^{-k(T_r''-1)} = 0 \qquad (4\text{-}19)$$

and this yields

$$A_{r3} + C_{r3}(1+ kT_r'') e^{-k(T_r''-1)} = 0 \qquad (4\text{-}19a)$$

Recalling the equation (4-1a) for the second and third virial coefficients,

$$\tau_{i1} = A_{ri} + B_{ri} + C_{ri} \qquad i = 2,3 \qquad (4\text{-}1a)$$

the constants of the second virial coefficient (A_{r2}, B_{r2}, C_{r2}) and the constants of the third virial coefficient (A_{r3}, B_{r3}, C_{r3}) are solved

similarly to each other and independently from the other constants by means of equations (4-1a), (4-17) and (4-18) or (4-19a), as follows,

$$B_{ri} = \frac{\Delta_{B_i}}{\Delta_i} \qquad i = 2,3 \qquad (4\text{-}20)$$

$$C_{ri} = \frac{\Delta_{C_i}}{\Delta_i} \qquad i = 2,3 \qquad (4\text{-}21)$$

and

$$A_{ri} = \tau_{i1} - B_{ri} - C_{ri} \qquad i = 2,3 \qquad (4\text{-}22)$$

Here,

$$\Delta_{Bi} = \begin{vmatrix} \lambda_i & \lambda_{C_i} \\ \mu_i & \mu_{C_i} \end{vmatrix} \qquad \Delta_{Ci} = \begin{vmatrix} \lambda_{B_i} & \lambda_i \\ \mu_{B_i} & \mu_i \end{vmatrix} \qquad \Delta_i = \begin{vmatrix} \lambda_{B_i} & \lambda_{C_i} \\ \mu_{B_i} & \mu_{C_i} \end{vmatrix} \qquad (4\text{-}23)$$

where

$$\lambda_{B2} = \lambda_{B3} = T_{B_r} - 1$$

$$\lambda_{C_2} = \lambda_{C3} = e^{-k(T_{Br}-1)} - 1$$

$$\lambda_2 = -\tau_{21}$$

$$\lambda_3 = \tau_{3B} - \tau_{31} = \frac{\gamma(T_B)}{Z_c^3} - \tau_{31}$$

$$\mu_{B2} = T_r' - 1$$

$$\mu_{B3} = -1$$

$$\mu_{C2} = e^{-k(T_r'-1)} - 1$$

$$\mu_{C3} = (1-kT_r'')\, e^{-k(T_r''-1)} - 1$$

$$\mu_2 = \tau_2' - \tau_{21} = -(1-Z_c)\left(\frac{T_r'}{Z_c}\right)^2 - \tau_{21}$$

$$\mu_3 = -\tau_{31} \qquad (4\text{-}24)$$

After all of the constants were determined it was necessary, by changing the parameters, to test the equation with experimental PvT data in order to refine the equation. Fortunately, the effects of the parameters were more regular than the parameters used for the critical isotherm, although the entire PvT surface was considered. At low densities, small changes in T_{Br} and T_r' greatly effect the percentage deviation, Dev. %, equation (4-14). The effect of the T_{Br} increases with temperature, but T_r' is more effective at low temperatures (Figures 13a, b). However, τ_{3B} is more important at high temperatures than T_r'', but T_r'' is effective at low temperatures (Figures 14a,b).

In Figures 13a, b and 14a, b, ($\nearrow$) or ($\searrow$) represents an increase or a decrease on the Dev. %, respectively. The numbers near the arrows in the figures show the order of the magnitude of the Δ(Dev. %).

b) The Slope and Curvature of the Isometrics. The equation of state, equation (3-34), by rearranging, may be written as follows,

$$P_r = A_r(v_r) + B_r(v_r)\, T_r + C_r(v_r)\, e^{-k(T_r-1)} \qquad (4\text{-}25)$$

where

$$A_r(v_r) = \sum_{i=1}^{7} \frac{A_{ri}}{\phi_i(v_r)} \qquad (4\text{-}25a)$$

$$B_r(v_r) = \sum_{i=1}^{7} \frac{B_{ri}}{\phi_i(v_r)} \qquad (4\text{-}25b)$$

$$C_r(v_r) = \sum_{i=1}^{7} \frac{C_{ri}}{\phi_i(v_r)} \qquad (4\text{-}25c)$$

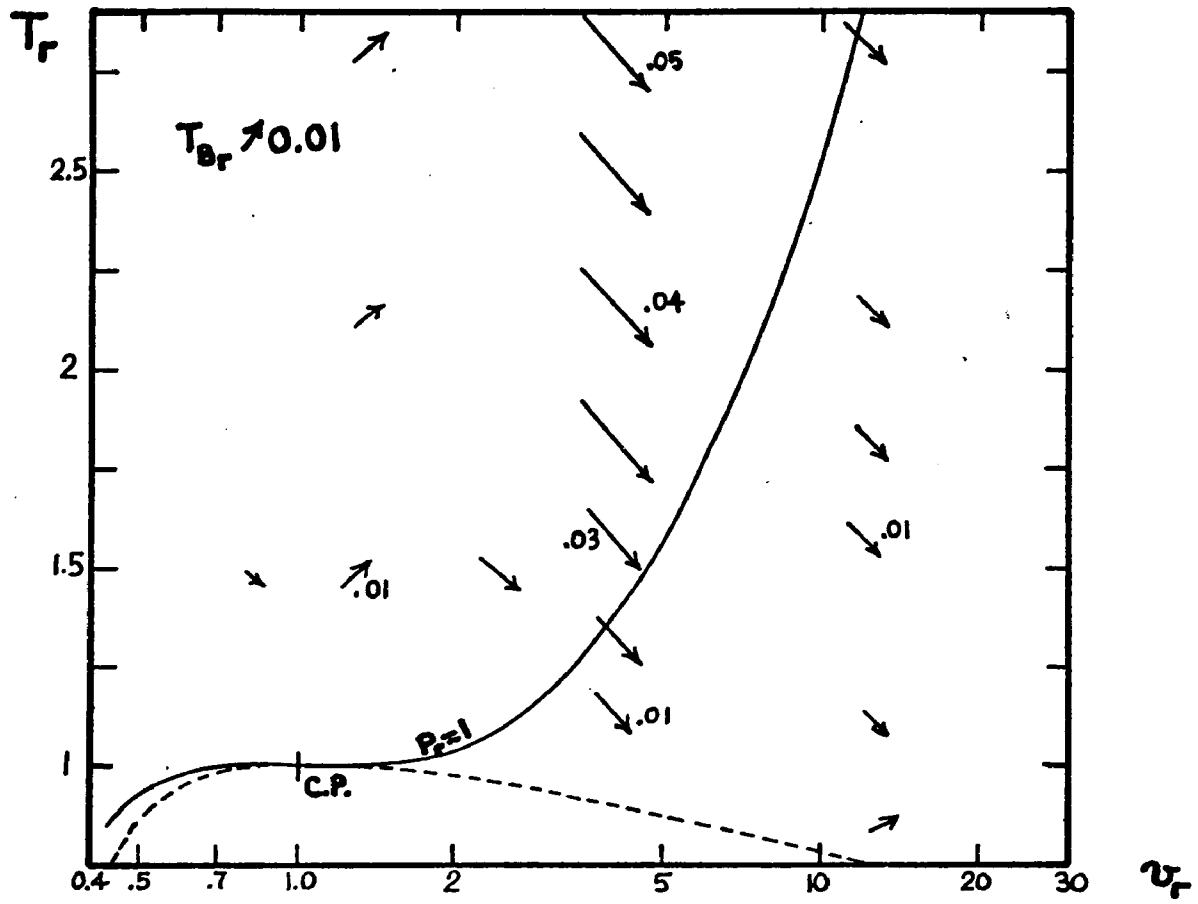


Figure 13a. The effect of the T_{Br} on the Dev. %

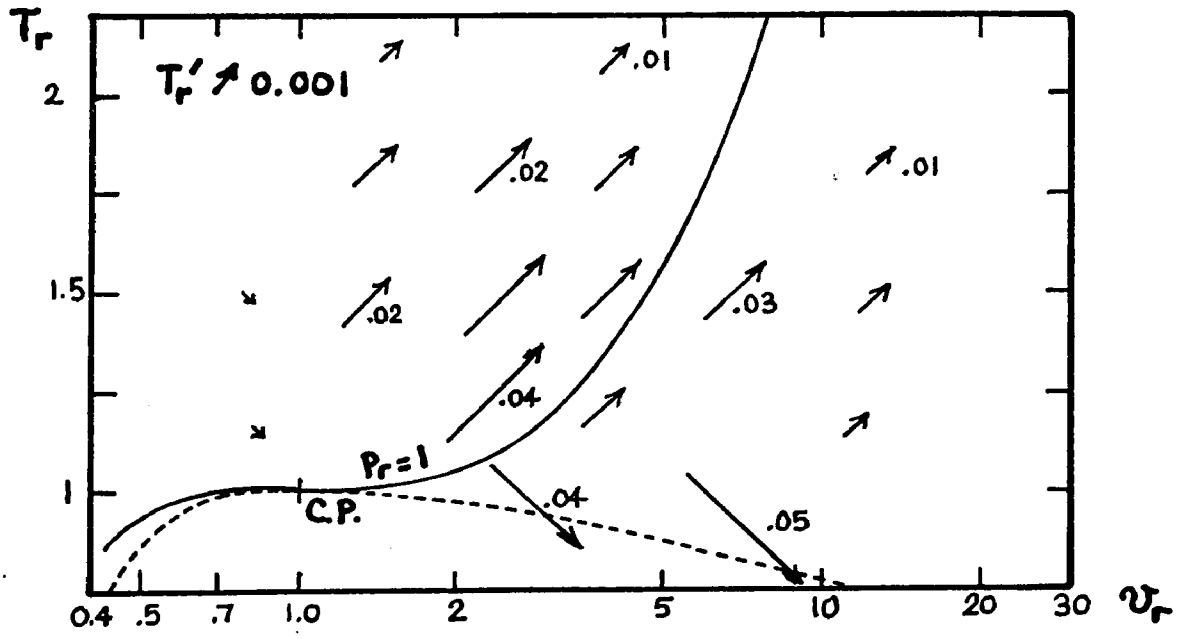


Figure 13b. The effect of the T_r' on the Dev. %

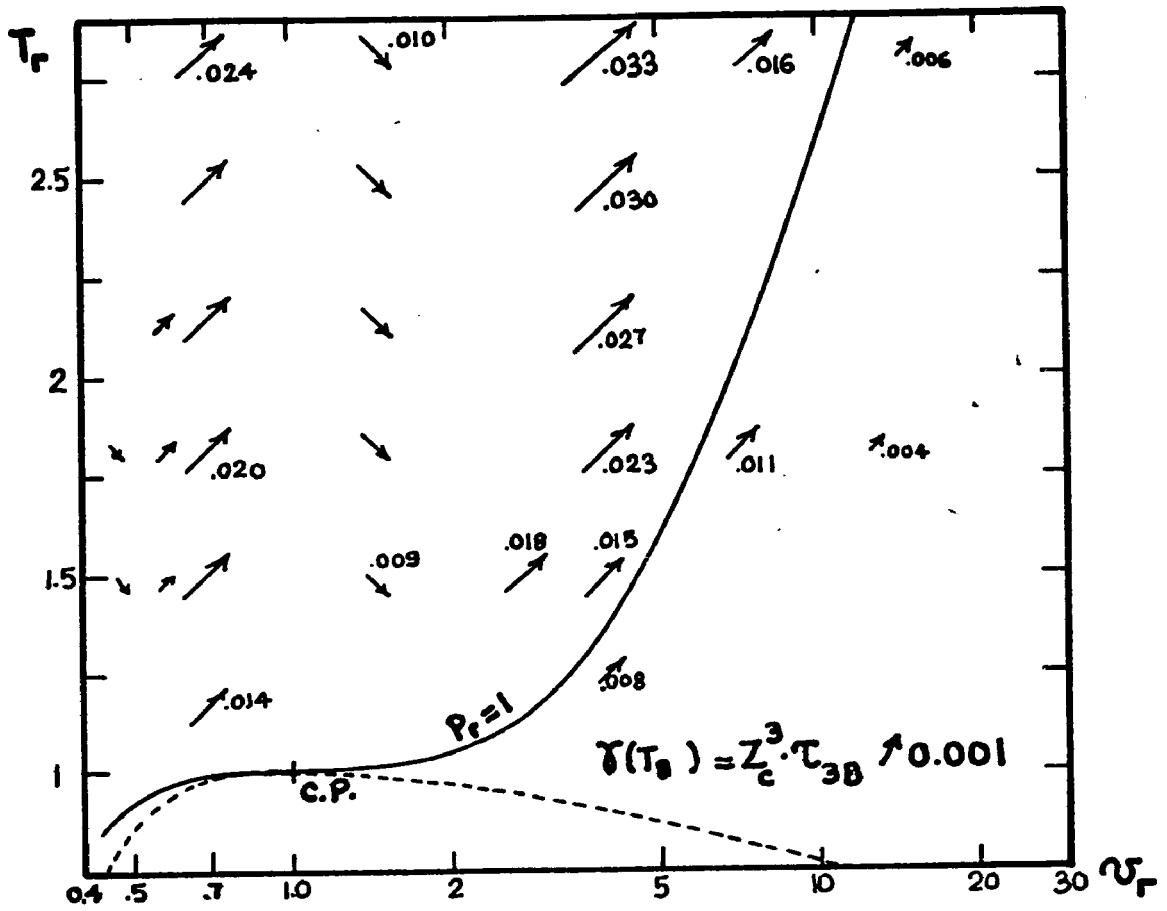


Figure 14a. The effect of the τ_{3B} on the Dev. %

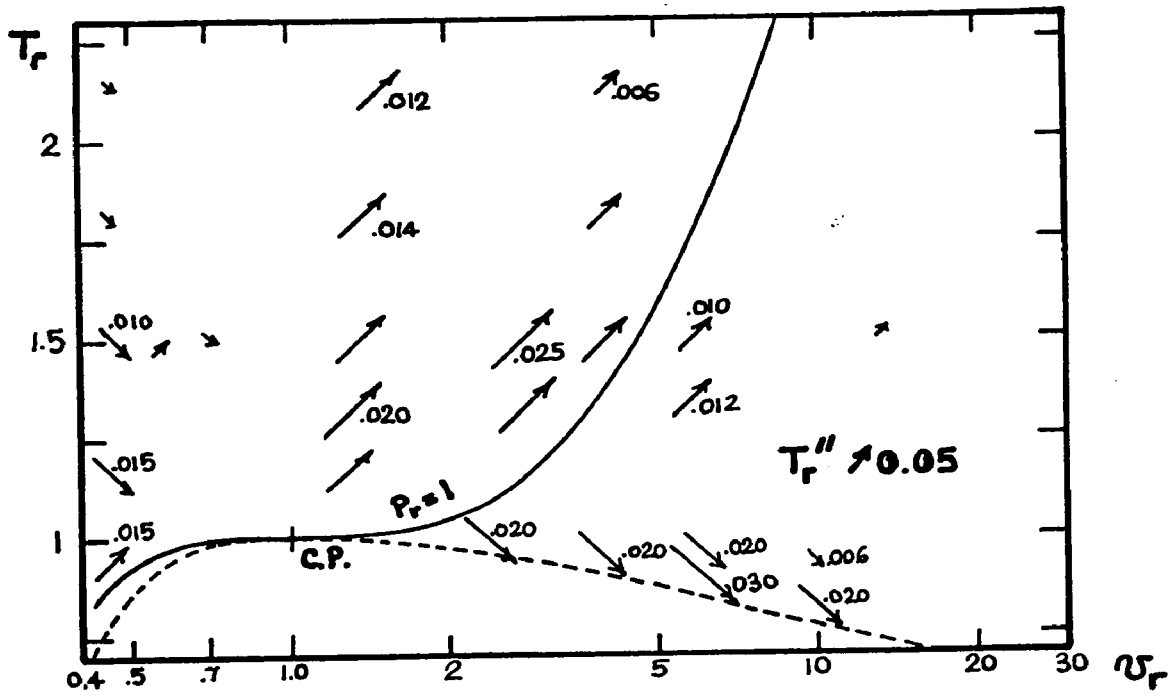


Figure 14b. The effect of the T_r''

and

$$\phi_i(v_r) = \begin{cases} v_r^i & i = 1,\ldots, 5 \\ e^{-\alpha_{ri}(v_r-1)} & i = 6,7 \end{cases} \qquad (4\text{-}25d)$$

By holding v_r constant, equation (4-25) expresses the isometrics. The exponential term, $e^{-k(T_r-1)}$, approaches zero as the temperature increases. This yields the fact that isometrics are nearly a straight line at high temperatures. Although the behavior of the isometrics at very high temperature (isometrics curve down) is not consistent with the equation of state, our primary attention in this work was focused near the critical region. Therefore, it was not necessary to add another term for this curvature at very high temperatures.

The first and second derivatives of the equation (4-25) with respect to reduced temperature produce the following relationships:

$$\left(\frac{\partial P_r}{\partial T_r}\right)_{v_r} = B_r(v_r) - k\, C_r(v_r)\, e^{-k(T_r-1)} \qquad (4\text{-}26)$$

$$\left(\frac{\partial^2 P_r}{\partial T_r^2}\right)_{v_r} = k^2\, C_r(v_r)\, e^{-k(T_r-1)} \qquad (4\text{-}27)$$

The properties of $C_r(v_r)$ are related to the constant volume specific heat (Chapter III, Part B.4). Combining equations (3-73) and (4-27) at the critical temperature, it may be concluded that $C_r(v_r)$ becomes zero at critical density and at the density ρ_{rx} between 1.8 and 2.0 times critical density (Figure 8). It is positive inside the density interval (1, ρ_{rx}) and negative outside the interval. Martin suggested the use of the densities ρ_{ry}, ρ_{rz} which are about 1.4 and 2.1 and their curvatures which are approximately $\frac{T_c^2}{100P_c}$ and $-\frac{T_c^2}{50\ P_c}$, respectively.

Thus, the relationships

$$C_r(v_r) = \begin{cases} 0 & \text{at } v_r = 1 \\ \dfrac{(T_c/k)^2}{C_y P_c} & \text{at } v_{ry} = \dfrac{1}{\rho_{ry}} \cong \dfrac{1}{1.4} \\ 0 & \text{at } v_{rx} = \dfrac{1}{\rho_{rx}} \cong \dfrac{1}{1.8} \\ -\dfrac{(T_c/k)^2}{C_z P_c} & \text{at } v_{rz} = \dfrac{1}{\rho_{rz}} \cong \dfrac{1}{2.1} \end{cases} \tag{4-28}$$

are written in order to determine C_4, C_5, C_6, and C_7. Here $C_y \cong 100$ and $C_z \cong 50$.

From the equation (4-26),

$$B_r(v_r) = m_r(v_r,T_r) + k\, C_r(v_r)\, e^{-k(T_r-1)} \tag{4-29}$$

and may be written. Here $m_r(v_r,T_r)$ is the slope of the isometrics. $B_r(v_r)$ is actually different than the slope of the isometrics; however, it approaches the slope as the temperature increases. On the other hand, $C_r(v_r)$ is a very small number, and is zero at the critical density and at the density $\rho_{rx} = 1.8$. Therefore, for the high temperatures, the equation

$$B_r(v_r) = m_r(v_r, T_r) \tag{4-30}$$

may be written. The following relations are proposed by Martin in order to determine B_4, B_5, B_6, and B_7:

$$B_r(v_r) = \begin{cases} m_{cr} & \text{at } v_r = 1 \\ C'_x \cdot m_{cr} & \text{at } v_{rx} = \dfrac{1}{\rho_{rx}} \cong \dfrac{1}{1.8} \\ C'_y \cdot m_{cr} & \text{at } v'_{ry} = \dfrac{1}{\rho'_{ry}} = \dfrac{1}{2.0} \\ C'_z/Z_c & \text{at } v'_{rz} = 1.5 \end{cases} \tag{4-31}$$

where m_{cr} is the slope of the critical isometric on P_r vs. T_r plot, $C'_x \cong 3.5$, $C'_y \cong 4.0$, $C'_z \cong 1.0$. After B_4, B_5, B_6, B_7 and C_4, C_5, C_6, C_7 are found by means of the fourth order linear matrices, A_4, A_5, A_6 and A_7 are obtained from the equations (4-1a).

Figures 15a through d and 16a through f illustrate the manner in which the percentage deviation, Dev. %, changes in different density regions when one of the parameters [used for the determination of the constants of the equation of state, equations (4-28) and (4-31)] is modified. The arrows (↑) or (↓) refer to an increase or a decrease, respectively, on the Dev. %, and the numbers give the order of magnitude of the Δ(Dev. %).

The parameters used for the curvature (Figures 15a through d) produce small changes, especially in the low temperature and high density range. The other parameters (m_{cr}, C'_x, C'_y, v_{rx}, v'_{ry} and v'_{rz}) used for the slope of the different isometrics are much more effective than the former parameters (Figures 16a through f). Their effect increases as temperature increases. Their effectiveness is very large in the high density region.

Although it has a large effect in the moderate density region up to critical density and in the density region higher than the critical up to 1.5 times critical density (in different directions) but not at high temperatures, in this work the curvature constant k was kept constant and was assumed to be the same for all substances (k=5.475).

First, T_{Br} and $\gamma(T_B)$ were varied in order to have a better fit at high temperatures and at low and moderate densities by using Figures 13a and 14a. Then, by using Figures 13b and 14b, the constants of the equa-

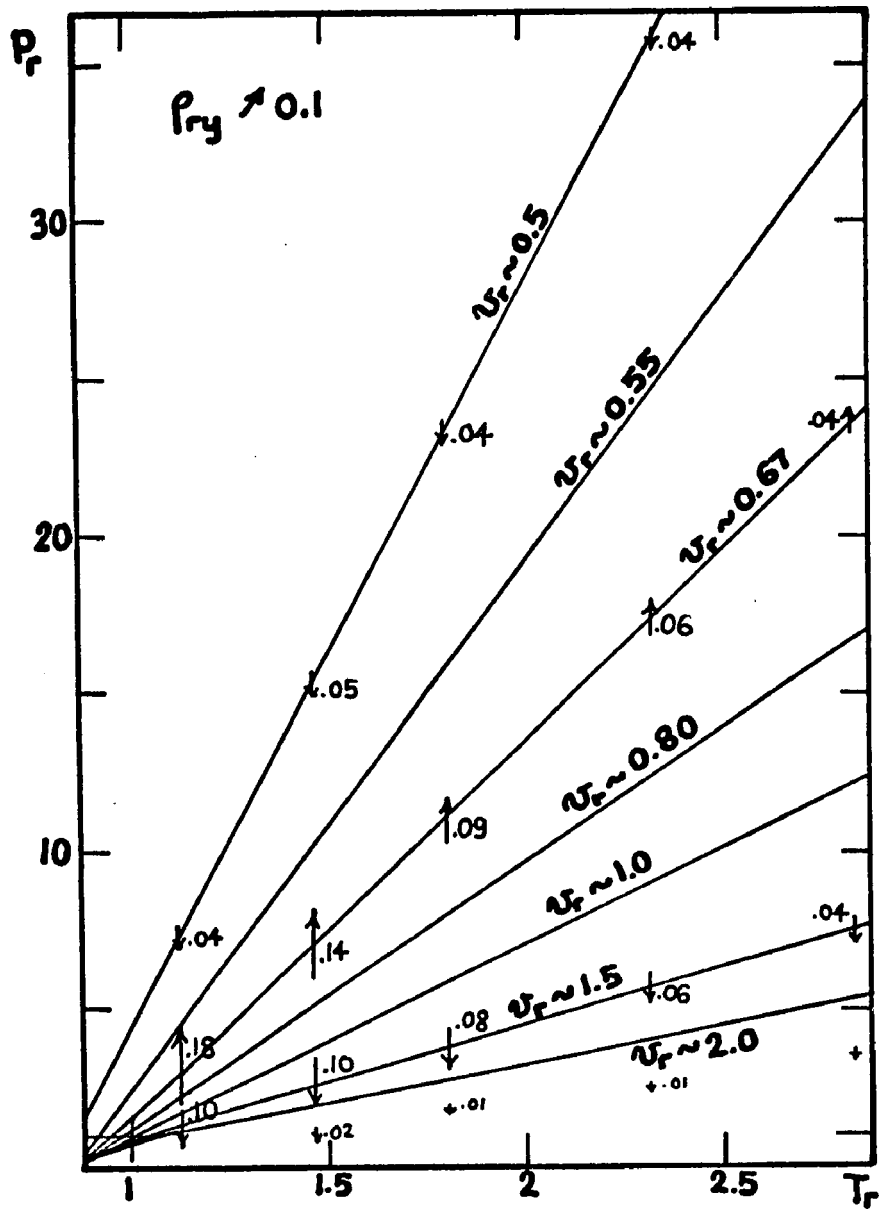


Figure 15a. The effect of the $\rho_{ry} \cong 1.4$

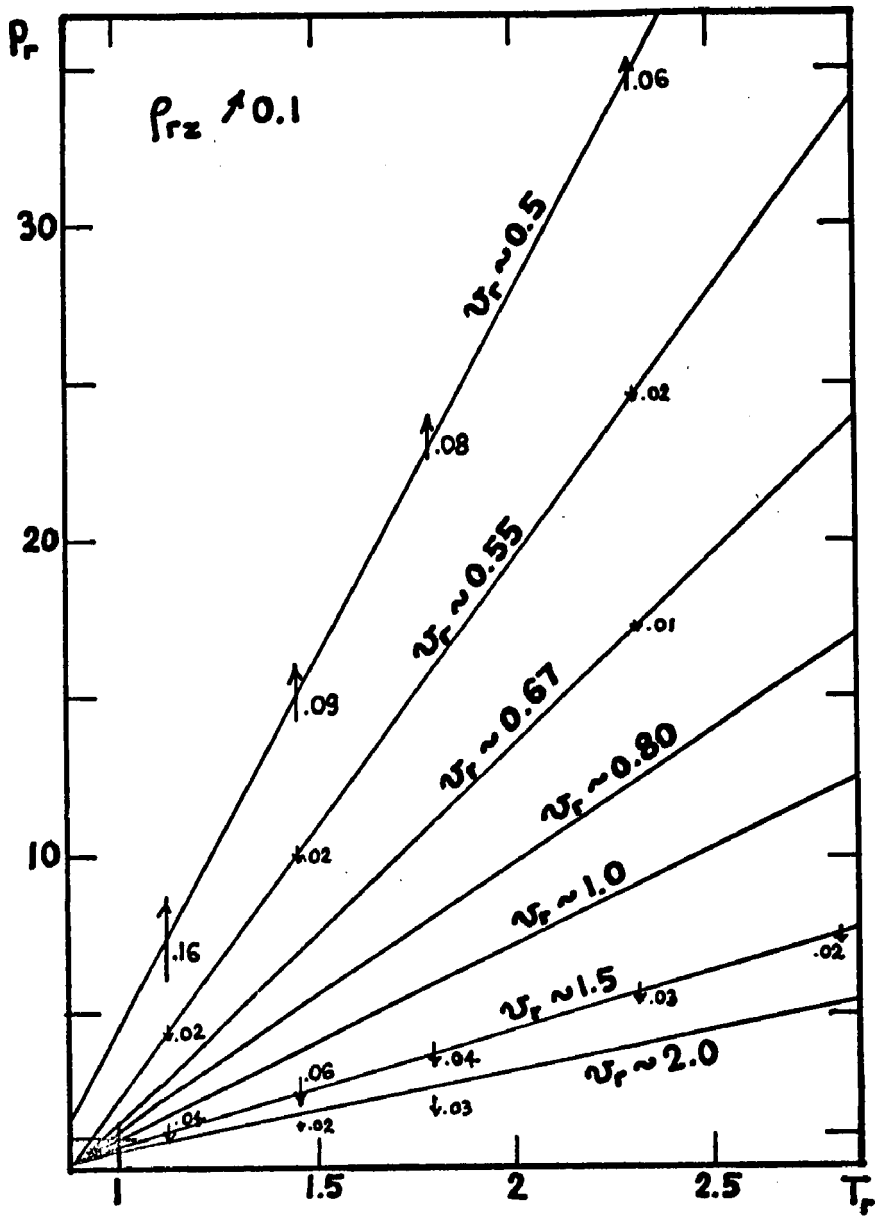


Figure 15b. The effect of the $\rho_{rz} \cong 2.1$

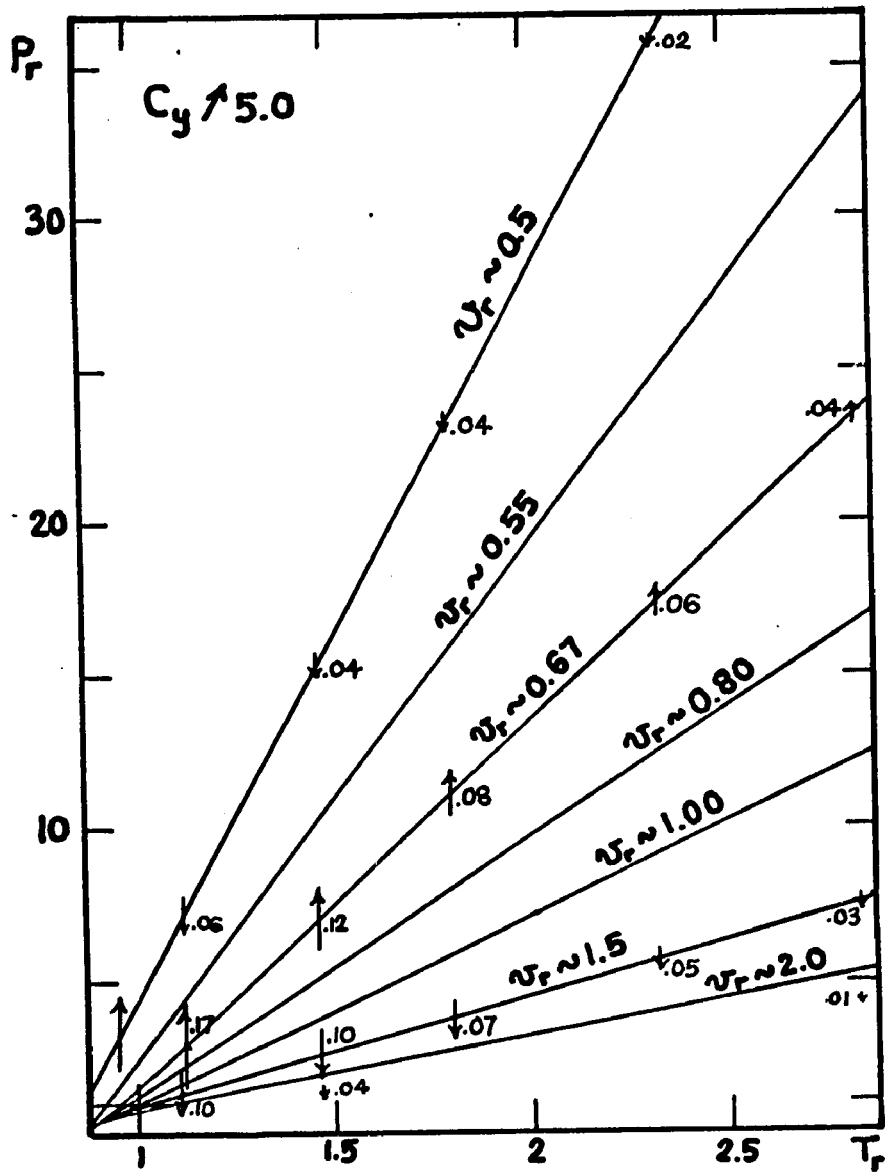


Figure 15c. The effect of the curvature of the $\rho_{ry} \cong 1.4$

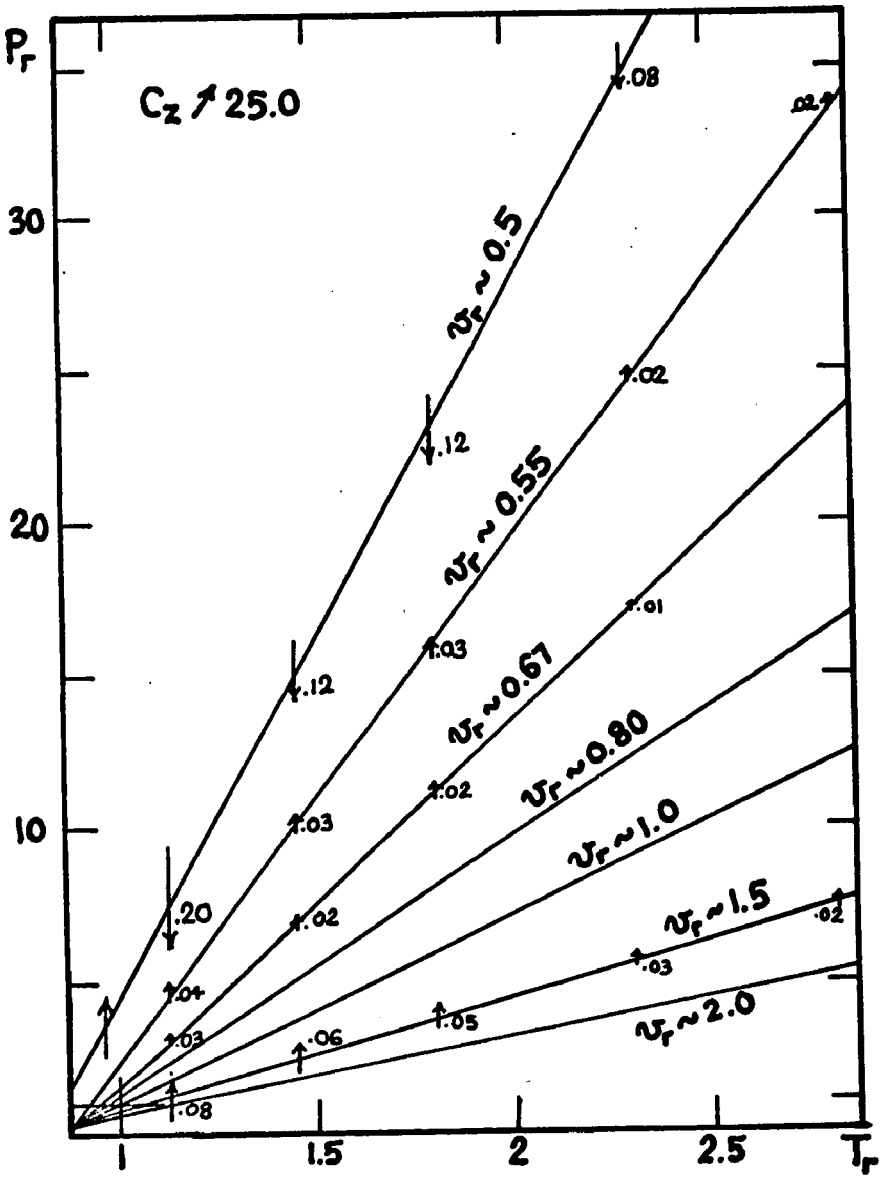


Figure 15d. The effect of the curvature of the $\rho_{rz} \cong 2.1$

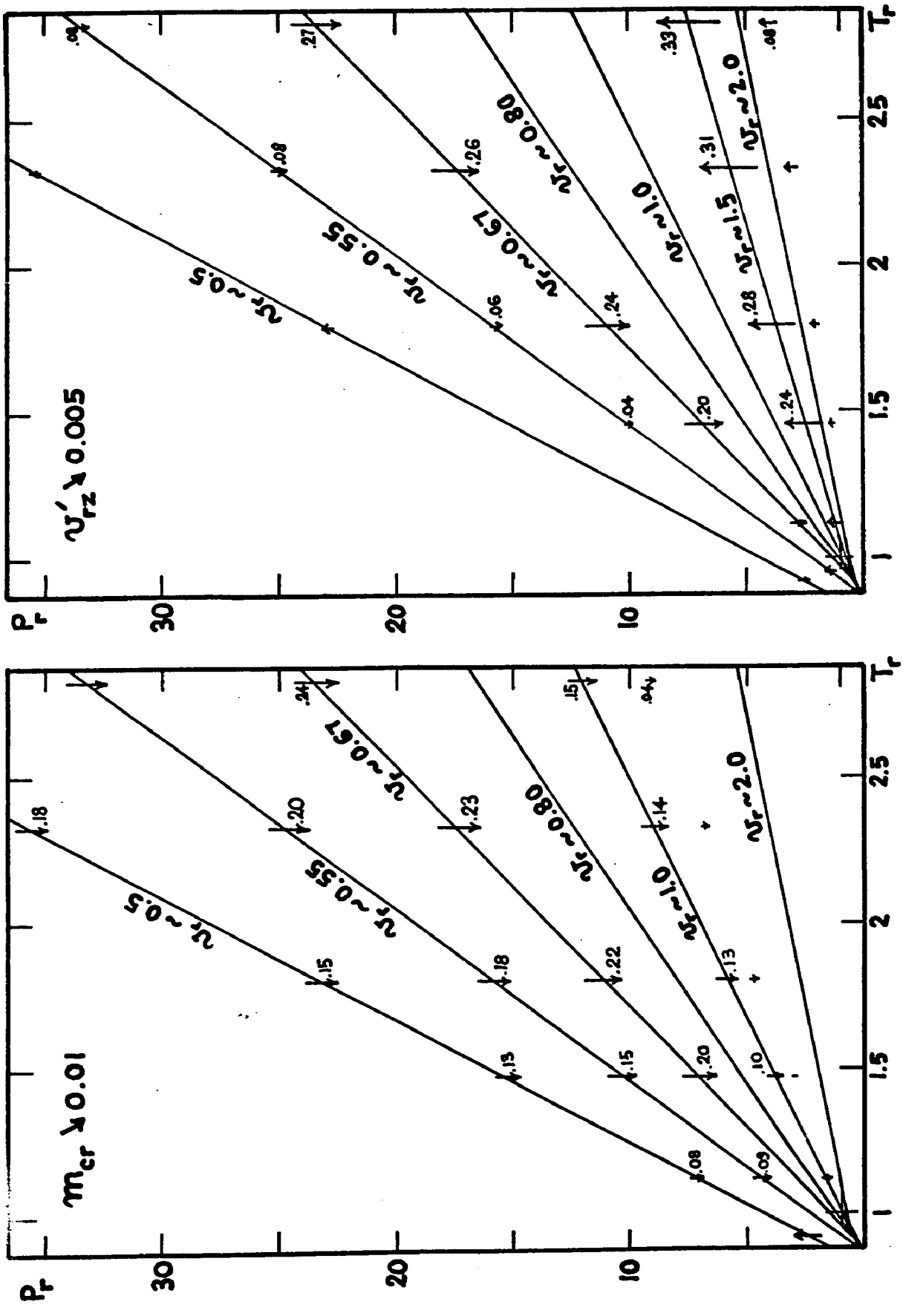


Figure 16a. The effect of the slope of the critical isometric, m_{cr}

Figure 16b. The effect of the ν'_{rz}

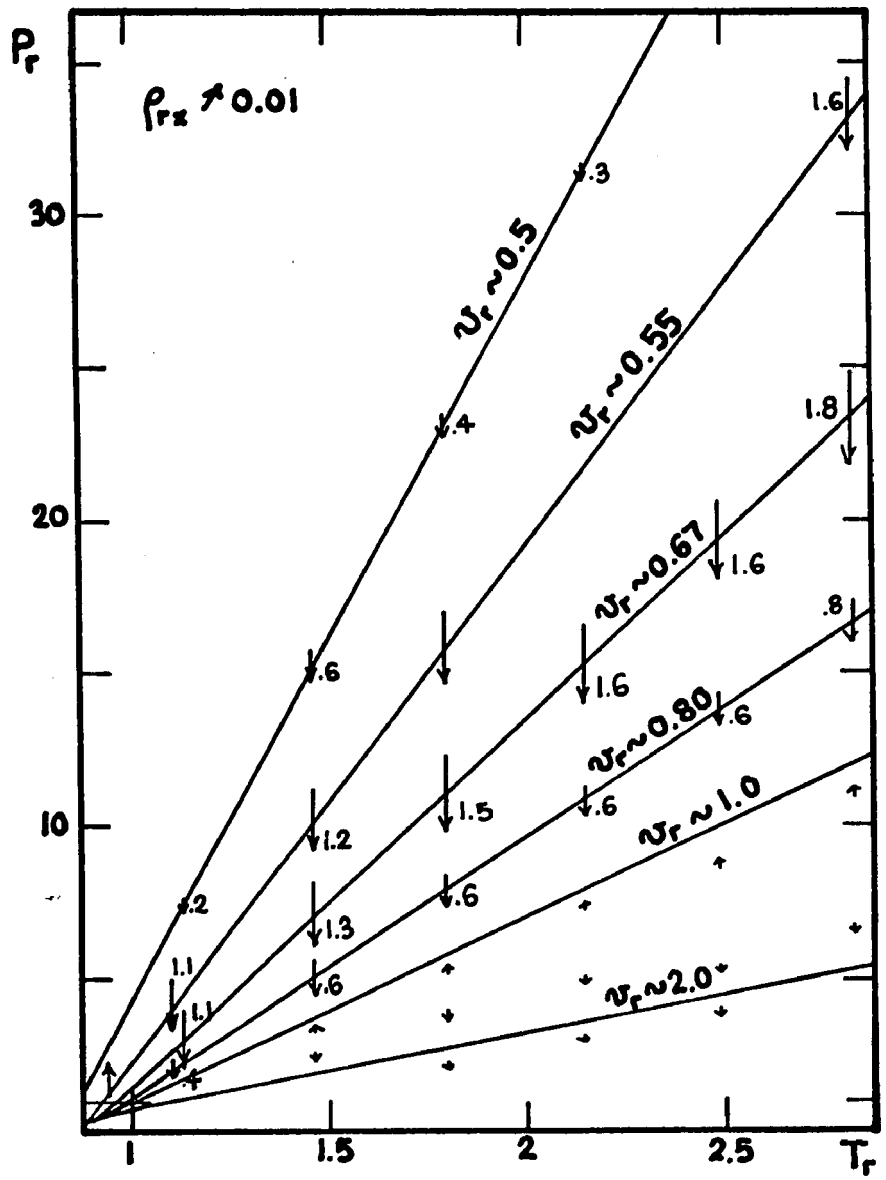


Figure 16c. The effect of the ρ_{rx}

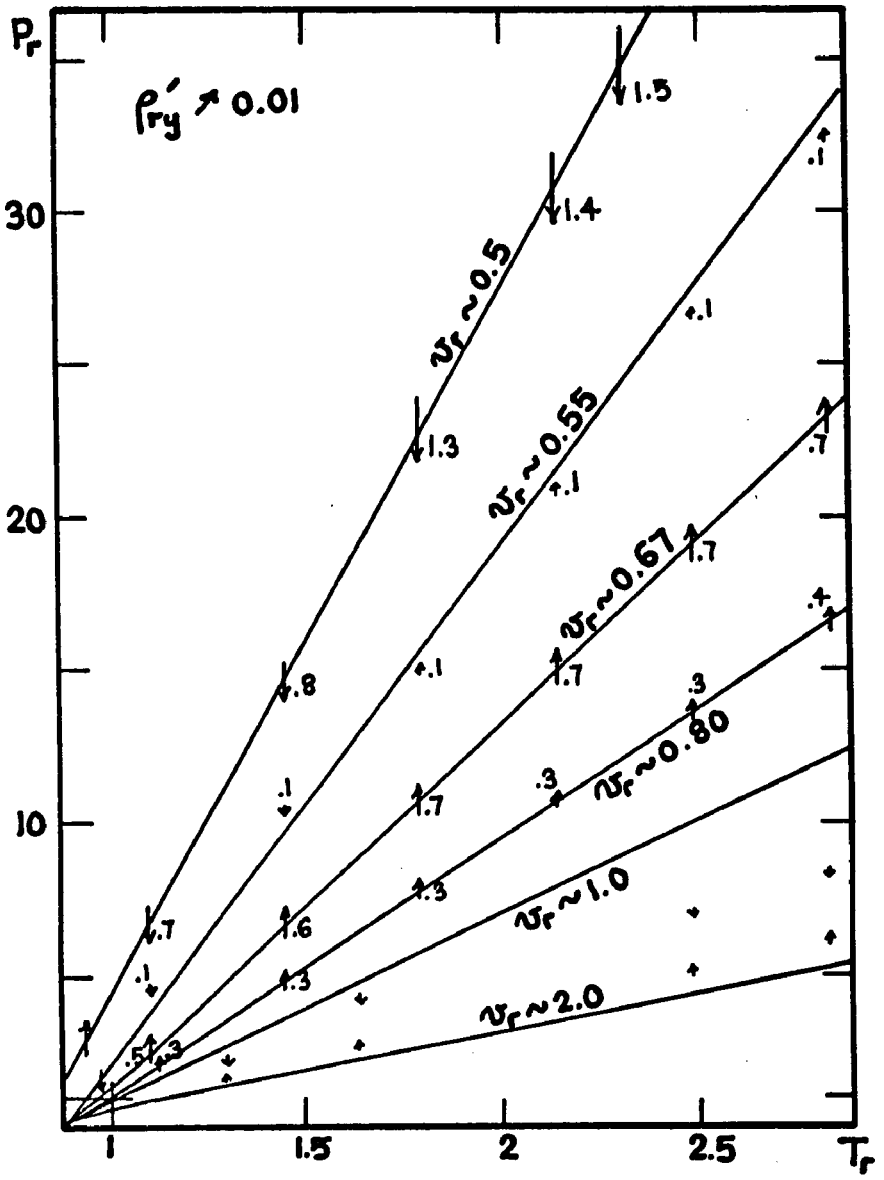


Figure 16d. The effect of the ρ'_{ry}

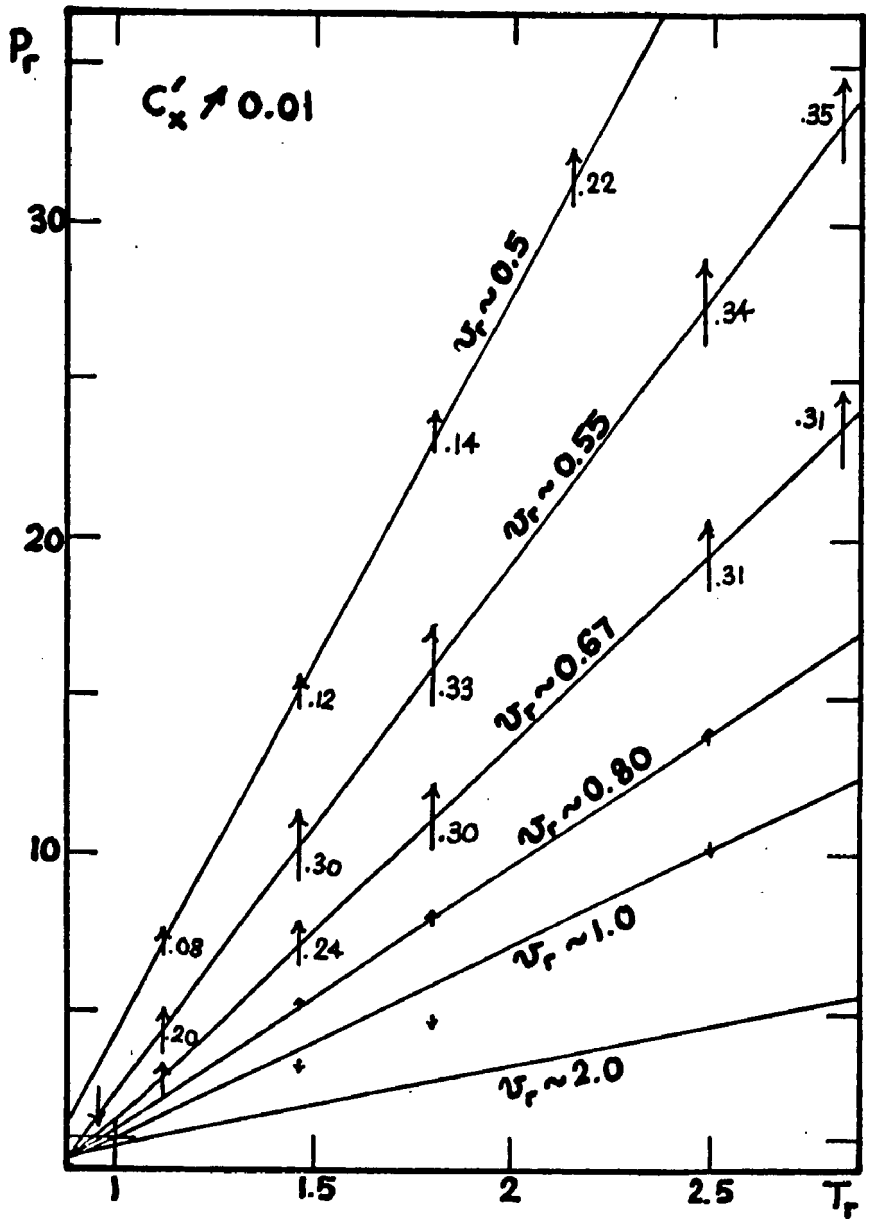


Figure 16e. The effect of the C_x' (the slope of the $\rho_{rx} \cong 1.8$)

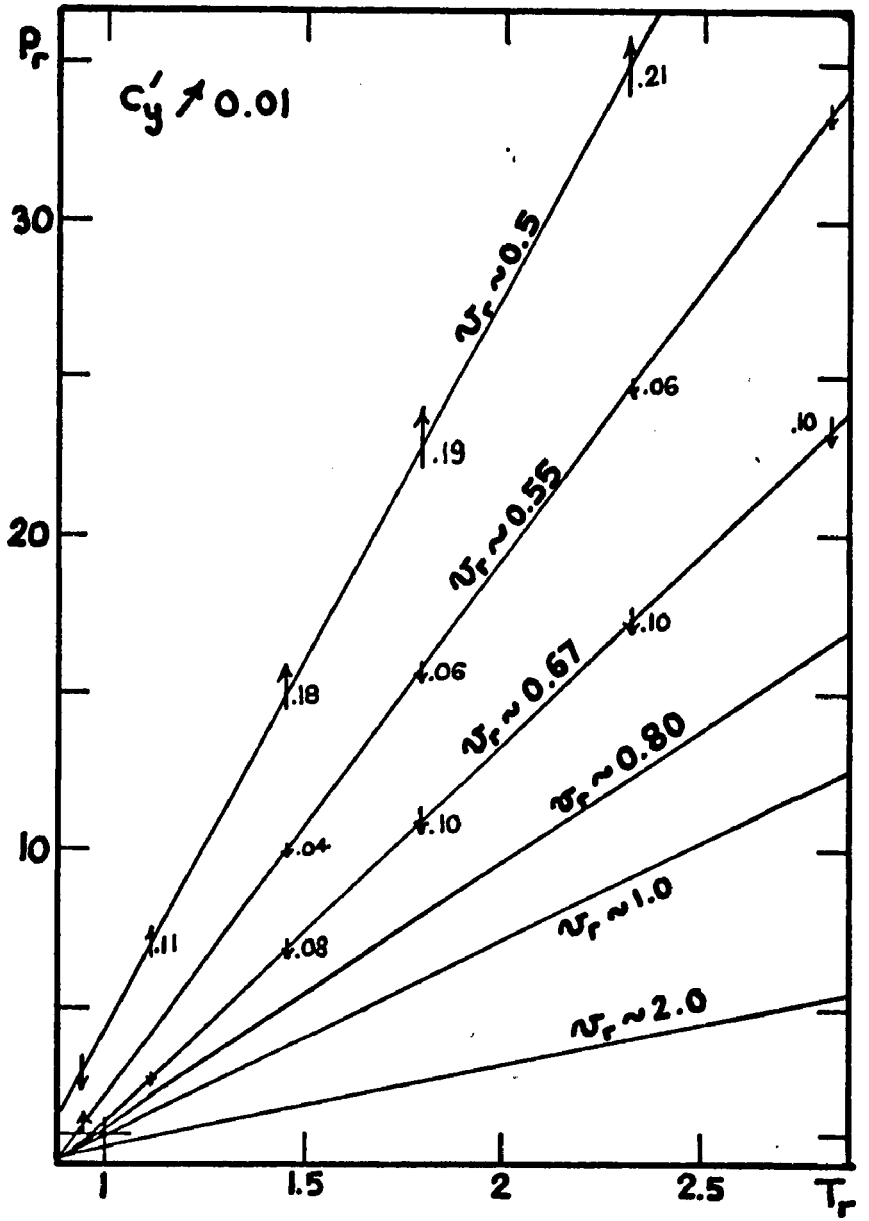


Figure 16f. The effect of the C_y' (the slope of the $\rho_{ry}' \cong 2.0$)

tion of state were adjusted for low temperatures and for low and moderate densities by means of T'_r and T''_r, respectively. By using the effect of m_{cr} (Figure 16a) the critical isometric coincided precisely with the experimental data. The effect of the ρ_{rx} and its slope coefficient, C'_x, and the effect of the ρ'_{ry} and its slope coefficient, C'_y, [equation (4-31)] are very important at the densities $\rho_{rx} \cong 1.8$ and $\rho'_{ry} \cong 2.0$; therefore, the high density region of the equation of state was fit to the experimental data by first using Figures 16c and e and Figures 16d and f simultaneously. Then the high density region was refined with the effect of the curvature parameters (ρ_{ry} and C_y, ρ_{rz} and C_z) because their effectiveness is more important in low temperature rather than high temperature regions (Figures 15a through d). However, these latter parameters made some changes in the density region less than critical ($1 < v_r < 2$); these undesirable changes were eliminated as much as possible by means of v'_{rz} (Figure 16b). Then, according to the results of the Dev. % in the overall region, the same procedure was applied successively in order to get better results.

The numerical values of the final parameters used in order to obtain the constants of the equation of state for argon, neon, and nitrogen are listed in Table XIV. Table XV-1 gives the reduced constants which are determined by means of these parameters. The constants may be calculated from equations (3-35a, b, and c) using the critical constants listed in Table II,(Table XV-2).

In appendices I-1,2,3, the calculated results by means of the equation of state equation (3-34), including the experimental data and the deviation from the experimental data whose sources and regions were tabulated previously in Table I, are given as computed with the computer.

TABLE XIV

PARAMETERS FOR ARGON, NEON, AND NITROGEN

	ARGON	NEON	NITROGEN
β_1	-0.3337	-0.3252	-0.3360
ε_3	-2.56	-2.77	-1.91
ε_4	40.3	41.3	27.3
α_{r6}	8.790	8.885	9.083
α_{r7}/α_{r6}	1.85	1.85	1.70
k	5.475	5.475	5.475
T_{Br}	2.620	2.620	2.500
T'_r	0.776	0.777	0.787
$\gamma(T_B)$	0.0120	0.0115	0.0125
T''_r	0.840	0.840	0.820
ρ_{rx}	1.845	1.845	1.830
ρ_{ry}	1.43	1.43	1.44
ρ_{rz}	2.20	2.26	2.22
C_y	110.00	100.00	100.00
C_z	55.00	70.00	50.00
m_{cr}	6.05	5.85	6.20
ρ'_{ry}	2.08	2.03	2.07
v'_{rz}	1.484	1.504	1.496
C'_x	3.45	3.40	3.40
C'_y	4.45	4.25	4.50
C'_z	1.00	1.00	1.00

TABLE XV-1

THE REDUCED CONSTANTS OF THE EQUATION OF STATE

CONST.	ARGON	NEON	NITROGEN
$B_{r1} = 1/Z_c$	0.3434722x10	0.3332603x10	0.3430992x10
A_{r2}	-0.5971846x10	-0.5421801x10	-0.6069069x10
B_{r2}	0.2279344x10	0.2069404x10	0.2427662x10
C_{r2}	-0.2442619	-0.2593550	-0.3138865
A_{r3}	0.1813519x10	0.1311094x10	0.2208117x10
B_{r3}	-0.2059304	-0.0747662	-0.3783737
C_{r3}	-0.1348870	-0.0975173	-0.1501387
A_{r4}	-0.2065622x10	-0.4392625x10	-0.2402857x10
B_{r4}	0.1582401x10	0.3318498x10	0.1294164x10
C_{r4}	0.3723926	0.1057867x10	0.06038380x10
A_{r5}	0.1440616x10	0.4286957x10	0.1215963x10
B_{r5}	-0.1308746x10	-0.3312717x10	-0.0704270x10
C_{r5}	0.0717007	-0.7542806	-0.09124547
A_{r6}	-0.2658315	-0.6275799	-0.1514978
B_{r6}	0.2665886	0.5118225	0.1289183
C_{r6}	$-0.6462431 \times 10^{-1}$	0.5203829×10^{-1}	$-0.4862538 \times 10^{-1}$
A_{r7}	$-0.0834534 \times 10^{-2}$	$-0.6045260 \times 10^{-2}$	$-0.06598292 \times 10^{-2}$
B_{r7}	0.1619041×10^{-2}	0.5154882×10^{-2}	$0.09061960 \times 10^{-2}$
C_{r7}	$-0.03201119 \times 10^{-2}$	0.1246293×10^{-2}	$.0058044 \times 10^{-2}$
α_{r6}	0.8790000x10	0.8884999x10	0.9082999x10
α_{r7}	0.1626149×10^{2}	0.1643724×10^{2}	0.1544110×10^{2}
k	5.475	5.475	5.475

TABLE XV-2

THE CONSTANTS OF THE EQUATION OF STATE

CONST.	ARGON	NEON	NITROGEN
$B_1 = R$	82.0597	82.0597	82.0597
A_2	-0.1604821×10^7	-0.02474381×10^7	-0.1650502×10^7
B_2	0.4060260×10^4	0.2127086×10^4	0.5231461×10^4
C_2	-0.6564075×10^5	-0.1183635×10^5	-0.8536244×10^5
A_3	0.3633675×10^8	0.0249776×10^8	0.5410546×10^8
B_3	-0.2735082×10^5	-0.0320804×10^5	-0.7346500×10^5
C_3	-0.2702677×10^7	-0.0185780×10^7	-0.3678846×10^7
A_4	$-0.3085892 \times 10^{10}$	$-0.0349329 \times 10^{10}$	$-0.5304828 \times 10^{10}$
B_4	0.1567012×10^8	0.0594387×10^8	0.2263984×10^8
C_4	0.0556328×10^{10}	0.0084128×10^{10}	0.1333104×10^{10}
A_5	0.1604662×10^{12}	$0.01423160 \times 10^{12}$	0.2418737×10^{12}
B_5	$-0.0966311 \times 10^{10}$	$-0.0247689 \times 10^{10}$	$-0.1110063 \times 10^{10}$
C_5	0.0798654×10^{11}	$-0.02504018 \times 10^{11}$	$-0.1815012 \times 10^{11}$
A_6	-0.1285029×10^2	-0.1643629×10^2	-0.05075177×10^2
B_6	0.0854228	0.3019060	0.03422157
C_6	-0.3123939×10	0.1362882×10	-0.1628950×10
A_7	-0.0403414	-0.1583253	-0.022104
B_7	0.0518788×10^{-2}	0.3040682×10^{-2}	0.0240551×10^{-2}
C_7	$-0.1547420 \times 10^{-1}$	0.3264039×10^{-1}	0.0194448×10^{-1}
α_6	0.1178916	0.2128450	0.1008102
α_7	0.2180994	0.3937630	0.1713773
k	5.475	5.475	5.475

P: atm. v: cc/mole, T: K

The beauty of the equation of state and the technique used to determine the constants is in its approach to better results. The results, the best obtained in this work, are not final and there is ample opportunity to achieve better outcomes with new constants. Perhaps future research in this area can be done for further improvements in the equation of state itself or for further calculations in order to determine other thermodynamic properties. However, the main purpose of this research was to apply the equation of state to mixtures.

C. THE CONSTANTS FOR THE MIXTURES

As mentioned previously (Chapter III, Part A), the form of the equation of state for mixtures would be the same as those of the pure components and the constants of the equation would be correlated with the corresponding constants of pure components, as functions of mole fractions.

Perhaps, first of all, as done previously by many investigators, the different combining rules (Chapter III, Part A.2) could be applied to each constant and the equation could be tested with the experimental PvT data in order to get the best agreement. However, if one of the three combinations (linear, square-root, and Lorentz) was tried with each constant, the tremendous amount (3^{20}) of combinations to be tested would indeed necessitate a vast amount of work. Therefore, in this work, this kind of evaluation of the mixture constants was avoided.

On the other hand, a different approach which was derived previously by assuming a linear combination between the reduced virial coefficients of a mixture and its pure components at a reduced temperature [equation (3-94)] might be considered. That assumption yielded

the result that the compressibility of the mixture at a given reduced temperature and reduced specific volume might be determined from the compressibilities of the pure components with linear interpolation [equation (3-95)]. Thus, a new combining rule for the reduced constants, which was much simpler in application and testing than the former approach, was derived for the constants, A_{ri}'s, B_{ri}'s, and C_{ri}'s (i = 2,...5). Although the derivation of a similar combining rule for the other constants was not able to be obtained by the same procedure, in this work the same combining rule was used for all A_{ri}'s, B_{ri}'s, and C_{ri}'s as follows,

$$Z_{cm}K_{rm} = \sum_{j=1}^{N} y_i Z_{cj} K_{rj} \qquad (4\text{-}32)$$

where Z_{cm} is the pseudo-critical compressibility of the mixtures. Z_{cm} may be determined from equation (3-95) by substituting T_r=1 and v_r=1, such that the equation derived is the same as equation (3-96a)

$$Z_{cm} = \sum_{j=1}^{N} y_j Z_{cj} \qquad (3\text{-}96a)$$

The constants α_{r6} and α_{r7} which are used in the exponential terms were combined by the linear combining rule,

$$\alpha_{mi} = \sum_{j=1}^{N} y_j \, \alpha_{rji} \qquad i = 6,7 \qquad (4\text{-}33)$$

It is, of course, necessary to correlate two of the pseudo-critical constants of the mixture (T_{cm}, v_{cm}, P_{cm}) in order to be able to estimate the volumetric properties of the mixture.

The linear combining rule was used for the pseudo-critical volume [equation (3-96b)]. Then, the linear [equation (3-96c)] and the linear square root [equation (3-97b)] combining rules were applied to the pseudo-critical temperature in order to compare the results.

The pseudo-critical pressure was determined from the equation $P_{cm}v_{cm} = Z_{cm}RT_{cm}$.

If the non-reduced constants are needed for equation (3-33) for mixtures, they may be calculated similarly to equations 3-35a, b, and c, by means of pseudo-critical constants.

CHAPTER V

EXPERIMENTAL METHOD AND APPARATUS

A. FINAL EXPANSION METHOD

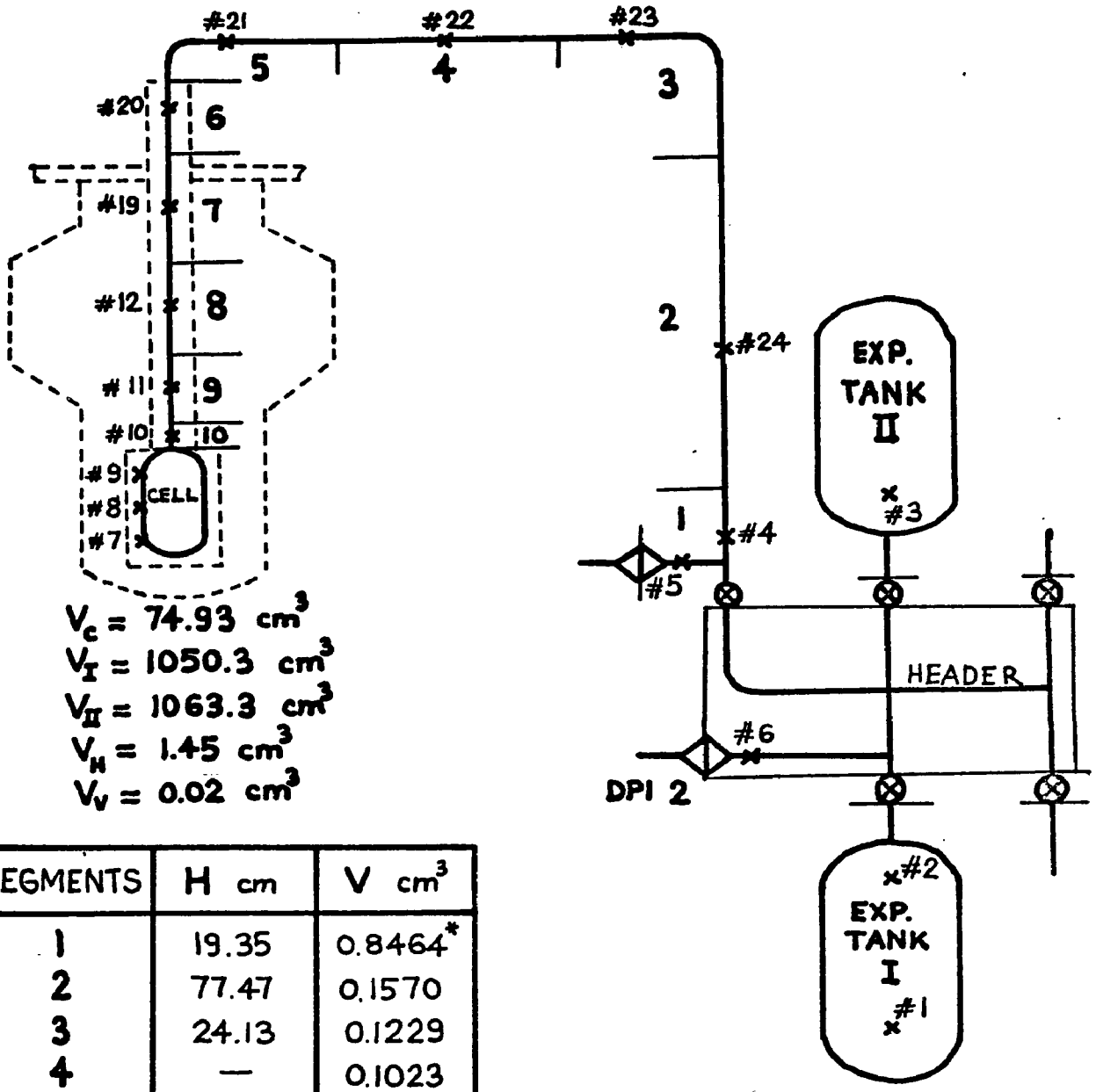
1. General. The final expansion method consists of measuring the mass of the fluid in the test cell by two successive expansions into two evacuated expansion tanks which are of much larger volume than the cell (Figure 17). The volumes of the cell and the expansion tanks, V_C, V_I, V_{II}, respectively, are known. After the first and second expansions the pressures and temperatures are measured.

This method was used previously by Scott and Sonntag (82) to measure PvT behavior of neon at low temperature and the method was compared with the other methods used to measure PvT data.

2. Theory of Mass Determination. After a series of temperature and pressure measurements of a substance in thermodynamic equilibrium at an approximately known density, the following technique is used to determine the mass of the fluid in the system: the fluid is first expanded into tank I which is evacuated, and the pressure is then measured at a certain temperature. After that, the second expansion is made into tank II, which was previously evacuated, and the pressure again measured at the same temperature. After the first expansion (subscript 1) and the second expansion (subscript 2), the following relation for the mass of the system may be written:

$$n = n_{C1} + n_{T1} + \sum n_{i1} = n_{C2} + n_{T2} + \sum n_{i2} \qquad (5\text{-}1)$$

where the number of moles and subscript C, T, i are cell, tank, and various segments along the tubes, respectively. Using the equation PV=nZRT,



SEGMENTS	H cm	V cm^3
1	19.35	0.8464*
2	77.47	0.1570
3	24.13	0.1229
4	—	0.1023
5	4.75	0.0843
6	17.78	0.0360
7	25.40	0.0515
8	20.32	0.0412
9	19.05	0.0386
10	5.08	0.0103

* Valve is open. When the valve is closed, 0.8358 cc.

Figure 17. The test cell and the expansion tanks location of thermocouples and segments

the equation (5-1) may be written as:

$$n = \frac{P_{C1}V_{C1}}{Z_{C1}RT_{C1}} + \frac{P_{T1}V_{T1}}{Z_{T1}RT_{T1}} + \sum \frac{P_{i1}V_i}{Z_{i1}RT_{i1}} = \frac{P_{C2}V_{C2}}{Z_{C2}RT_{C2}} + \frac{P_{T2}V_{T2}}{Z_{T2}RT_{T2}} + \sum \frac{P_{i2}V_i}{Z_{i2}RT_{i2}} \qquad (5\text{-}2)$$

where P is the pressure, V is the volume, Z is the compressibility, T is the temperature and R = 82.0597 atm-cc/mole-K is the universal gas constant. The pressures are subscripted differently because of the hydrostatic pressure difference at different locations due to elevation changes.

In equation (5-2), pressures, volumes, and temperatures are known but, in general, compressibilities are unknown. Some of these compressibilities (Z_{i1} and Z_{i2}) can be obtained from published data for pure substances or from the generalized compressibility chart using pseudo-critical constants for mixtures. This is actually satisfactory even if the values are not accurate because the contribution of $\sum n_{i1}$ or $\sum n_{i2}$ is very small when it is compared with other terms n_{C1}, n_{T1}, or n_{C2}, n_{T2}, respectively.

If $T \gg T_{critical}$ and $P \ll P_{critical}$, the compressibility factor, Z, may be determined accurately by

$$Z = 1 + B'(T) \cdot P \qquad (5\text{-}3)$$

where $B'(T) = \frac{B(T)}{RT}$ and B is the second virial coefficient. Scott and Sonntag (82) used equation (5-3) for the density measurement of neon. However, in this work, the maximum temperatures at which the fluid is expanded is not much greater than the pseudo-critical temperature of either the argon-neon or of the nitrogen-neon system; therefore, the compressibility might be written more accurately by

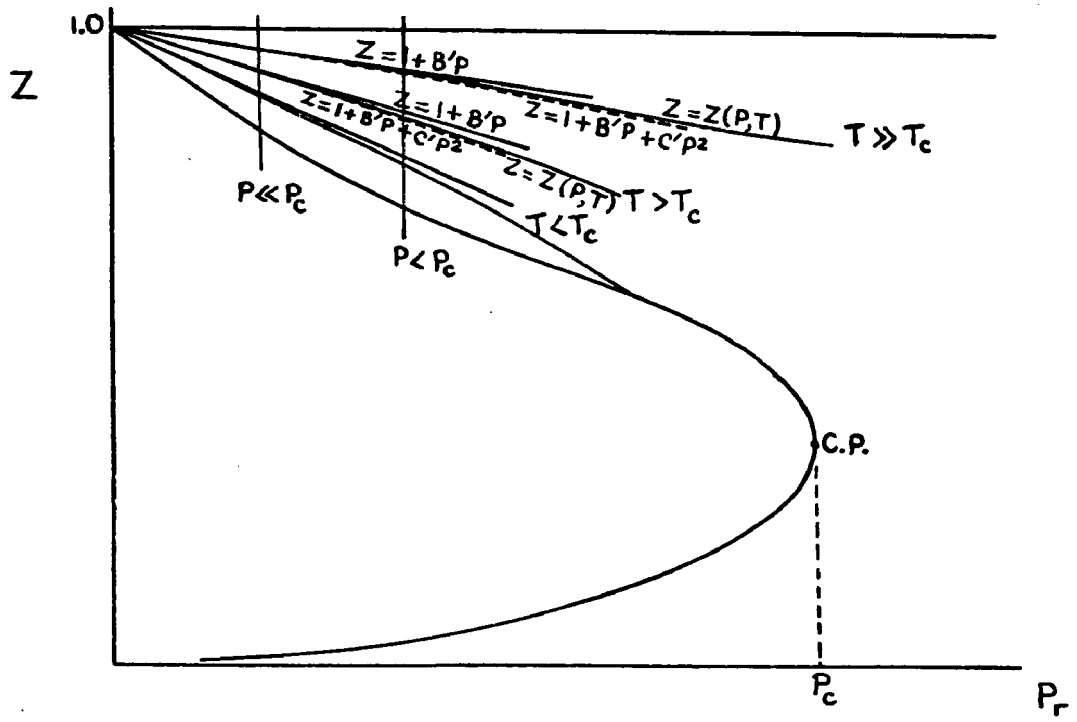


Figure 18. Compressibility approximation for low pressure

$$Z = 1 + B'(T) \cdot P + C'(T) \cdot P^2 \qquad (5\text{-}4)$$

where $B'(T) = \frac{B(T)}{RT}$, $C'(T) = \frac{C-B^2}{(RT)^2}$ and B and C are the second and third virial coefficients, respectively (Figure 18). Writing equation (4-4) for Z_{C1} and Z_{C2}

$$Z_{C1} = 1 + B'(T_{C1})\, P_1 + C'(T_{C1})P_1^2 \qquad (5\text{-}5)$$

$$Z_{C2} = 1 + B'(T_{C2}) \cdot P_2 + C'(T_{C2}) \cdot P_2^2 \qquad (5\text{-}6)$$

and eliminating B' between equations (5-5) and (5-6) because $T_{C1} \cong T_{C2}$:

$$Z_{C1} = 1 + \frac{P_{C1}}{P_{C2}} (Z_{C2}-1) + C'(T_C) \cdot (P_{C1}-P_{C2}) \cdot P_{C1} \qquad (5\text{-}7)$$

may be obtained. Substituting equation (5-7) into equation (5-2) and solving it to obtain Z_{C2}:

$$Z_{C2} = \alpha_1 + (\alpha_1^2 - \alpha_2)^{1/2} \qquad (5\text{-}8)$$

where

$$\alpha_1 = \frac{1}{2}\left\{\left[1 - \frac{P_{C2}}{P_{C1}} - C'(T_C)\cdot(P_{C1}-P_{C2})\cdot P_{C2}\right] + \frac{P_{C2}}{\delta}\left(\frac{V_{C2}}{T_{C2}} - \frac{V_{C1}}{T_{C1}}\right)\right\} \tag{5-9}$$

$$\alpha_2 = \frac{P_{C2}V_{C2}}{\delta T_{C2}}\left[1 - \frac{P_{C2}}{P_{C1}} - C'(T_C)\cdot(P_{C1}-P_{C2})\cdot P_{C2}\right] \tag{5-10}$$

$$\delta = \left(\frac{P_{T1}V_{T1}}{Z_{T1}T_{T1}} - \frac{P_{T2}V_{T2}}{Z_{T2}T_{T2}}\right) + \left(\sum \frac{P_{i1}V_i}{Z_{i1}T_{i1}} - \sum \frac{P_{i2}V_i}{Z_{i2}T_{i2}}\right) \tag{5-11}$$

Then Z_{C1} is obtained from equation (5-7).

The equation (5-4) may be used to determine the compressibilities in the expansion tanks as:

$$Z_{T1} = 1 + B'(T_{T1}) \cdot P_{T1} + C'(T_T1)\, P_{T1}^2 \tag{5-12}$$

$$Z_{T2} = 1 + B'(T_{T2})\, P_{T2} + C'(T_{T2})\, P_{T2}^2 \tag{5-13}$$

This also makes it possible to determine the mass in the tank. If the expansion tanks are filled with gas or with gas mixtures at low pressure ($P \ll P_{critical}$) and much higher than the critical (or the pseudo-critical) temperature, the mass may be calculated by:

$$n_T = \frac{P_T V_T}{[1+B'(T_T)\cdot P_T + C'(T_T)P_T^2]\cdot R\cdot T_T} \tag{5-14}$$

Thus, after measuring a series of temperatures and pressures at a constant mass of fluid, some of the substance is blown, at a low pressure, into one or two of the evacuated expansion tanks and then the mass is calculated by equation (5-14) by measuring the tank pressure and temperature.

3. The Determination of the Second and the Third Virial Coefficients for Ar-Ne and Ne-N_2 Mixtures. In order to be able to use equations (5-7), (5-12), and (5-13) to calculate the mass of the system it is necessary to know the value of the second and third virial coefficients of gas mixtures at the cell and tank temperatures. Those could be determined by the well-known theoretical combining rules, equations (3-4) and (3-5), for binary mixtures written as follows:

$$B_m = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \qquad (5\text{-}15)$$

$$C_m = y_1^3 C_{111} + 3y_1^2 y_2 C_{112} + 3y_1 y_2^2 C_{122} + y_2^3 C_{222} \qquad (5\text{-}16)$$

where y_1, y_2 are mole fractions of pure components, B_{11}, B_{22} and C_{111}, C_{222} are the second and third virial coefficients of pure components respectively, and B_{12} is the interaction second virial and C_{112}, C_{122} are the interaction third virial coefficients. The second and the third virial and the interaction second and third coefficients may be obtained in two ways: experimental or theoretical. The latter is the analytical integration of the virial coefficient integral for the Lennard-Jones (6-12) potential or for another potential function (44).

The values of the second virial and the interaction second virial coefficients used in this work were obtained from experimental data (16) (Figure 19), and then those values were compared with theoretical values that were derived for the Lennard-Jones (6-12) potential (44). There was a large difference between the two values of the interaction second virial coefficients (Table XVI). On the other hand, after finding Z_{C1} or Z_{C2} it was possible to get the second virial coefficients for the cell temperature by

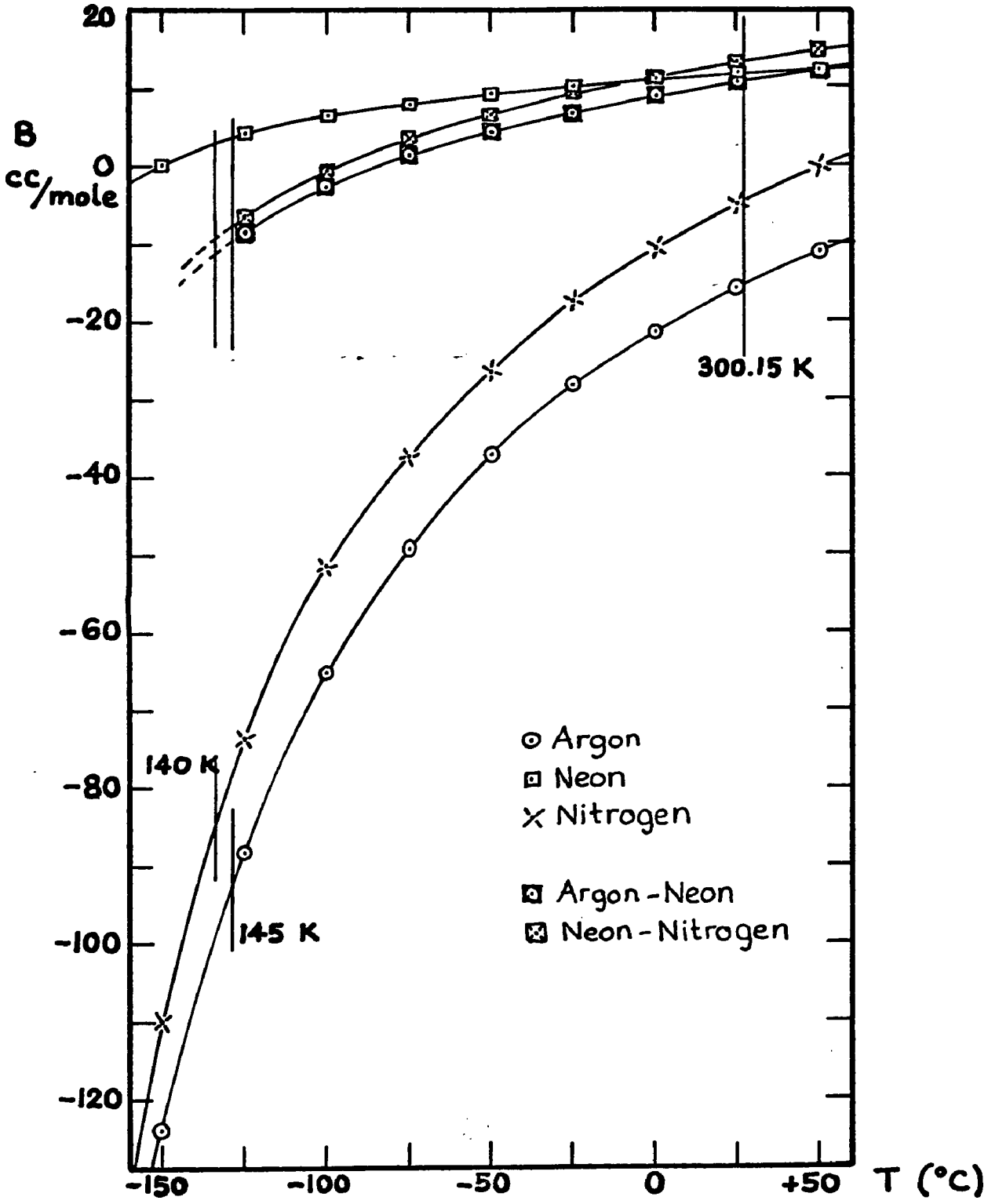


Figure 19. Second virial coefficients for Argon, Neon and Nitrogen, and interaction second virial coefficients for Argon-Neon and Neon-Nitrogen systems (16).

TABLE XVI. The values of the second and third virial coefficients at cell and tank temperatures

	ARGON-NEON 46.82%, 53.18%				NEON-NITROGEN 51.4% 48.6%			
	T ≈ 145 K		T ≈ 300.15 K		T ≈ 140 K		T ≈ 300.15 K	
	(16)	(44)	(16)	(44)	(16)	(44)	(16)	(44)
B_1 ($\frac{cc}{mole}$)	-92.20	-90.11	-15.30	-15.45	3.20	3.18	11.80	11.65
B_{12} "	-9.50 (-31.00)*	-17.00	11.00	7.64	-9.00 (-50.00)*	-14.91	13.40	11.15
B_2 "	3.80	3.79	11.80	11.65	-84.30	-79.48	-4.50	-4.33
C_1 ($\frac{cc}{mole}$)^2		1469.62		944.19		239.75		215.25
C_{112} "		794.16		561.04		492.09		421.50
C_{122} "		412.82		351.17		1039.01		777.83
C_2 "		238.19		215.25		2238.50		1409.05
B_m ($\frac{cc}{mole}$)	-34.57	-27.15	5.46	3.71	-44.05	-25.38	8.75	7.63
C_m ($\frac{cc}{mole}$)^2		628.39		464.99		857.49		636.63
$10^3 B'_m$ atm^{-1}	-2.91	-2.28	0.22	0.15	-3.83	-2.21	0.36	0.31
$10^6 C'_m$ atm^{-2}	-4.00	-0.77	0.72	0.74	-8.20	-1.62	[illegible]	0.95

(*) Obtained by means of equations (5-15) and (5-17)

$$B'(T_C) = \frac{Z_C - 1}{P} - C'(T) \cdot P \qquad (5\text{-}17)$$

where $B'(T) = \frac{B(T)}{RT}$, $C'(T) = \frac{C - B^2}{(RT)^2}$, Z_C is the compressibility at the cell temperature. By this way, the final PvT data were checked; it was found that the effect of the large difference of the interaction second virial coefficients at the cell temperature was negligibly small.

The values of the third and the interaction third virial coefficients were obtained only by the latter method (Table XVI).

B. EXPERIMENTAL APPARATUS:

The overall equipment used to measure the PvT behavior of the argon-neon and neon-nitrogen systems is shown in a schematic overview in Figure 20. The same system, in 1967, was previously used for neon between the temperatures 30-70 K by Scott and Sonntag (82) and,after some developments in the system, was also used for nitrogen in the temperature range 110-140 K by Sonntag and Öztürk (88).

To briefly summarize, the apparatus consists of a two-walled (in order to balance the pressures within the cell) stainless steel cell surrounded with an evacuated test package which is in the liquid nitrogen cryostat and of two stainless steel expansion tanks in the constant temperature oil bath. Temperature control is maintained by the electrical heating of several resistors at different locations around the test cell and by the cooling of liquid nitrogen around the evacuated test package in order not to have diffusive heat transfer between the liquid nitrogen and the test assembly. The temperatures in the cell and in the oil bath are measured using two platinum resistance thermometers and a Mueller bridge. Also many thermocouples (Figure 17) (#7 through #12 Cu-AuCo, others Cu-Con) are located along the stainless steel tube from the cell to the

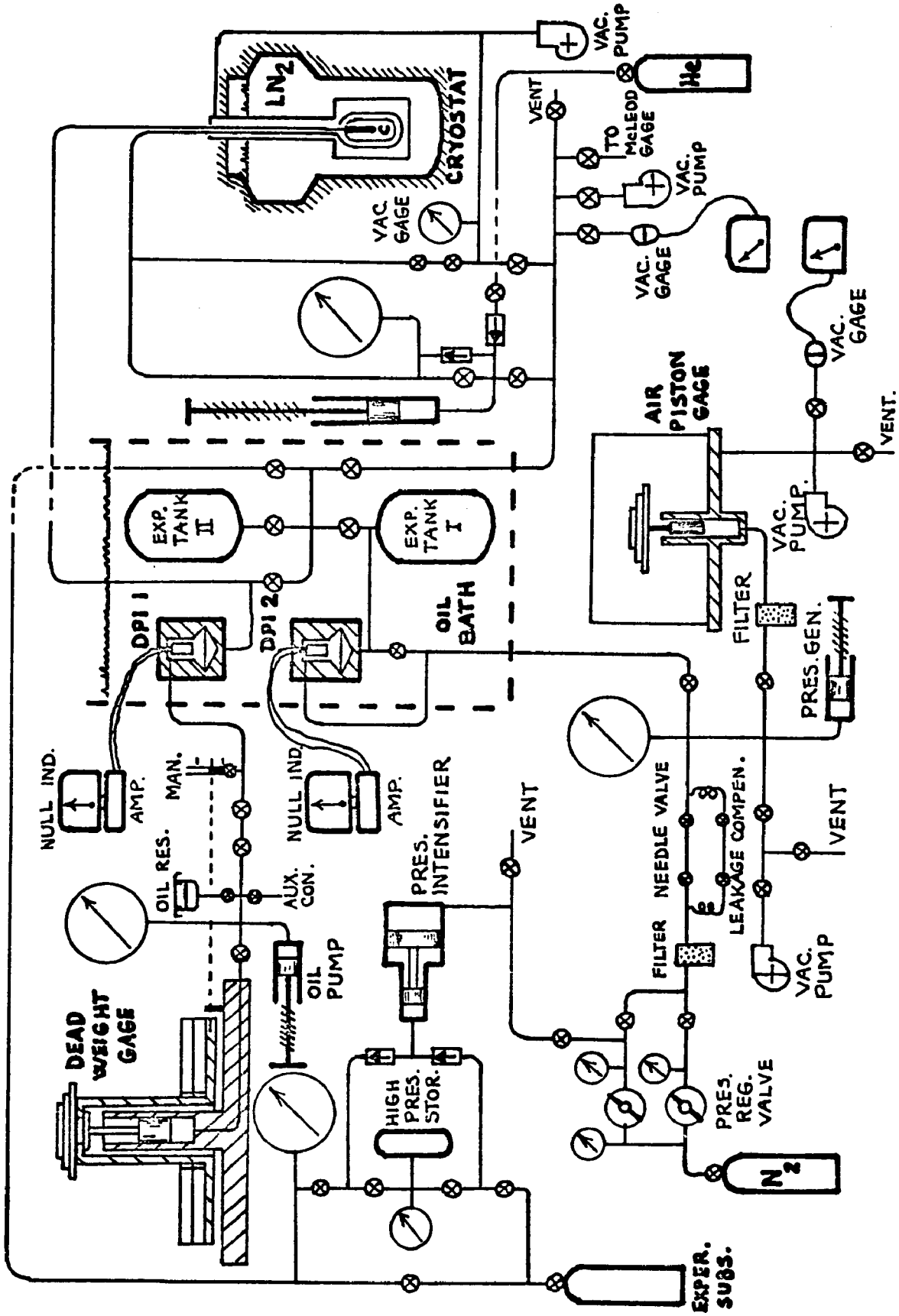


Figure 20. A schematic overview of the constant volume PvT measurement system

differential pressure indicator (DPI) to measure and to check the temperatures around the cell and in the oil bath. A dead weight gage (DWG) is used for the measurement of the cell pressure and an air piston gage (APG) is used to measure the pressure in the expansion tanks.

For further reference, a quite detailed and thorough description of the apparatus may be found in reference 82.

C. VOLUME MEASUREMENT

The volumes of the test cell, the expansion tanks, and the header were measured with a device whose schematic diagram is shown in Figure 21. The same kind of apparatus, in principle, had been used previously (82).

The device consists of high-precision diameter glass, measuring tubes, an evacuation system, a gas filling and a mercury supply system, a differential pressure indicator, and a platinum resistance thermometer.

The basic principle of the device is to move the gas in the measuring tubes (which is initially at ambient conditions), into a tank whose volume is unspecified by replacing the gas with mercury and then, to bring the gas back to its initial state. If ambient conditions, room pressure, and temperature do not change during the replacement process, V_M, the volume of mercury filled into the glass tubes, will be equal to the unknown volume, V_U.

Scott and Sonntag had used a mercury manometer with a high gain near zero to balance the system pressure to atmospheric pressure. The correction due to temperature differences between the initial and the final temperatures of the measuring tube and the volume measured was made using a perfect gas relation and it was assumed that the atmospheric pressure did not change. Thus, the equation,

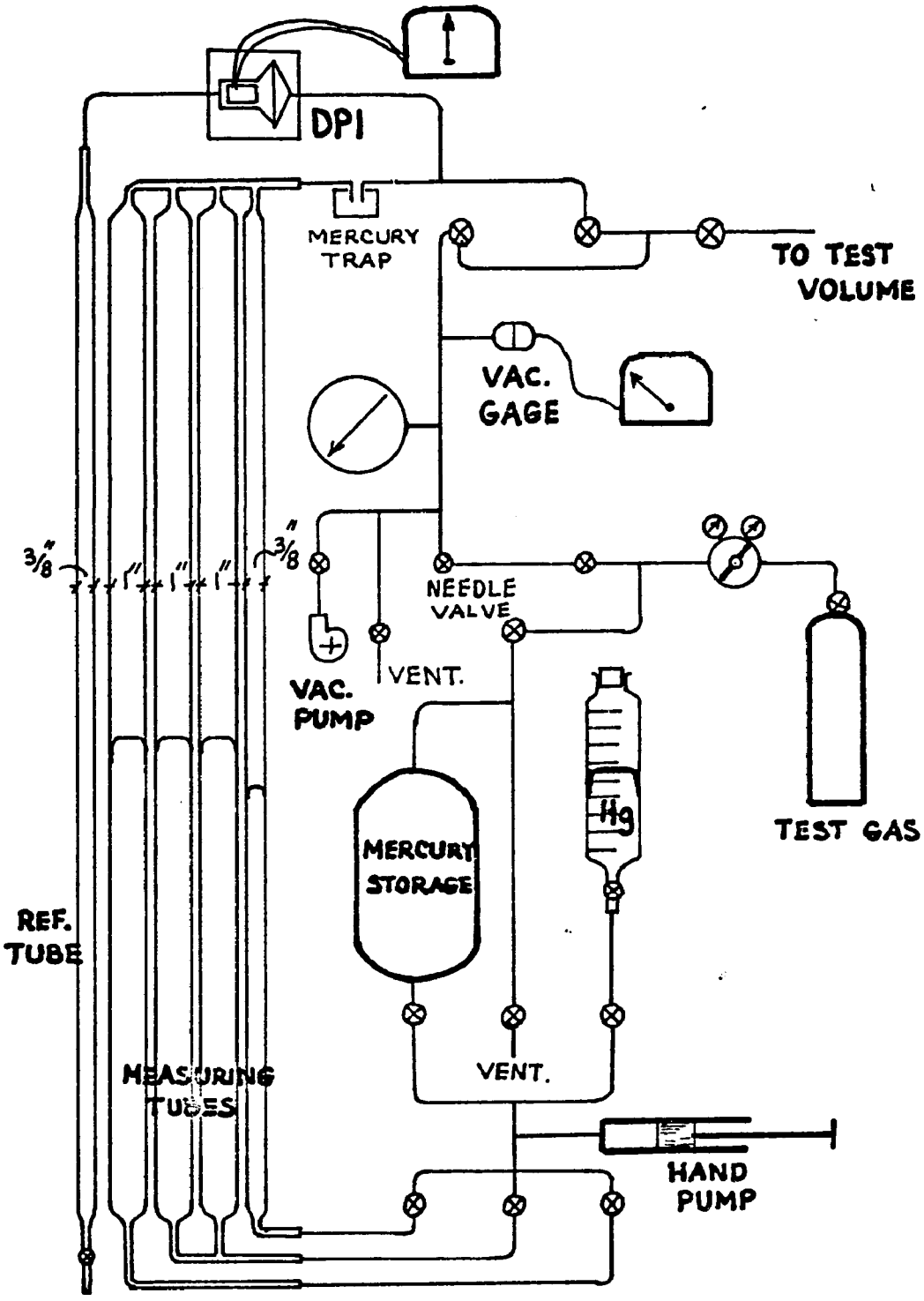


Figure 21. The schematic diagram of the volume measurement apparatus.

$$V_U = \frac{T_{2U}}{T_1} V_M + \left(\frac{T_{2U}}{T_1} - \frac{T_{2U}}{T_2}\right) V_o \qquad (5\text{-}18)$$

was used by Scott and Sonntag. Here V_U is the unknown volume, V_M is the volume filled with mercury, V_o is the volume above the mercury, T_1 is the initial and T_2 is the final temperature of the gas in and above the measuring tubes and T_{2U} is the temperature of the gas in the unspecified volume tank. It is pointed out that the magnitude of the volume above the mercury affects the result.

In the new device, the mercury manometer was replaced with a differential pressure indicator, Ruska Instrument Corporation, model 2416.5, cell s/m 13727, control box s/n 13641, in order to balance the system pressure more accurately with the reference pressure. Then a constant volume reference system, which is similar to and thermally in contact with the measuring tubes, was used to eliminate the effect of the change of atmospheric pressure (Figure 22). From the real gas relation,

$$n_{\substack{meas.\\sys}} R = P_1 \frac{V_M V_o}{Z_1 T_1} = P_2 \left(\frac{V_U}{Z_{2U} T_{2U}} + \frac{V_o}{Z_2 T_2}\right) \qquad (5\text{-}19)$$

and

$$n_{\substack{ref\\sys}} R = P_1 \frac{V_{ref}}{Z_1 T_1} = P_2 \frac{V_{ref}}{Z_2 T_2} \qquad (5\text{-}20)$$

may be written for the system in the measuring tubes and the reference system respectively. The notation is the same as in equation (5-18) and V_{ref} is the volume of the reference tube. Dividing equations (5-19) and (5-20) side-by-side and eliminating V_{ref},

$$V_U = \frac{Z_{2U}}{Z_2} \frac{T_{2U}}{T_2} V_M \qquad (5\text{-}21)$$

can be obtained. Actually, T_{2U} is very close to T_2, therefore it may be assumed that $Z_{2U} = Z_2$. Thus, equation (5-21) gives a simple relation,

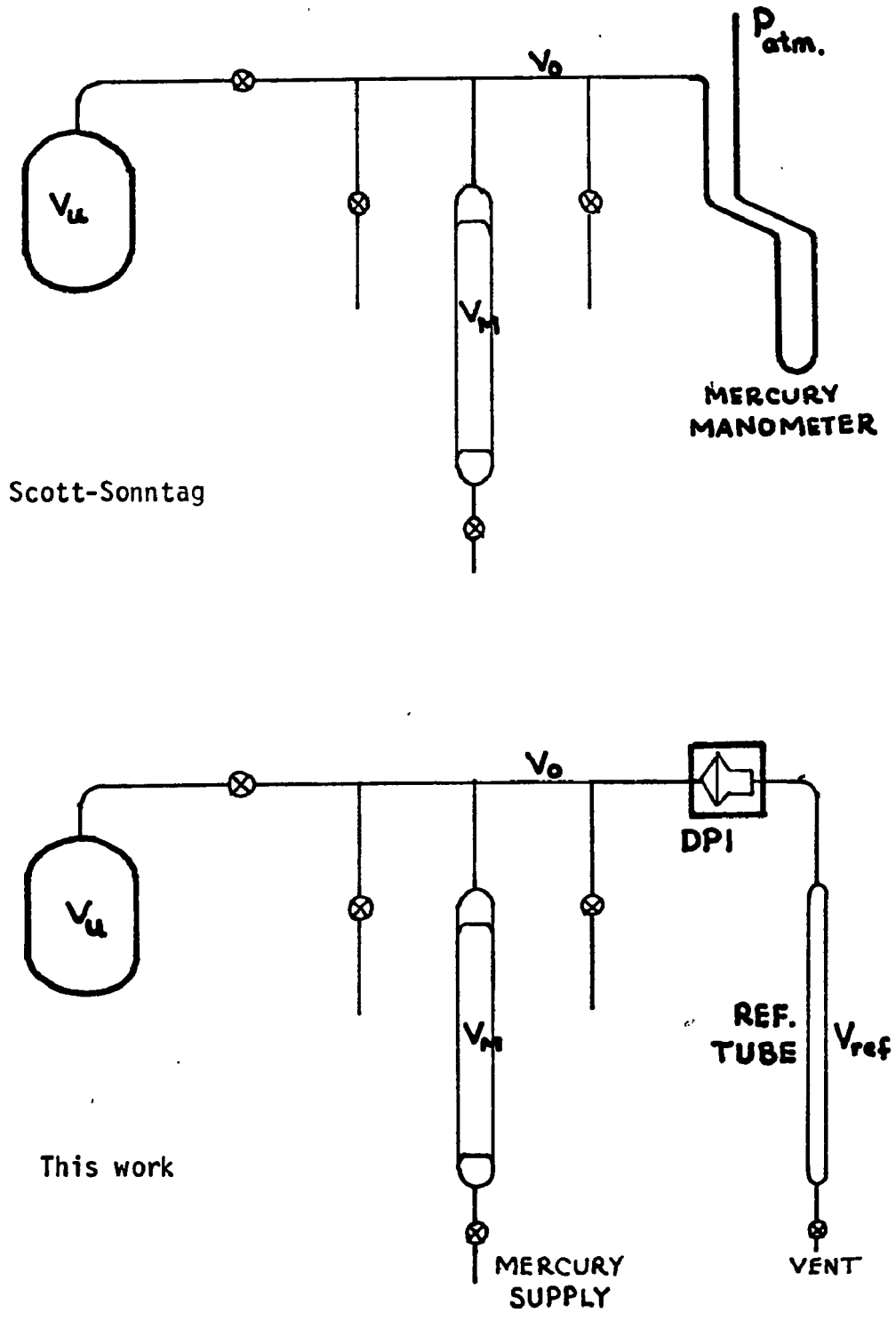


Figure 22. The comparison of the volume measurement device with Scott and Sonntag's (82).

$$V_U = \frac{T_{2U}}{T_2} V_M \qquad (5\text{-}22)$$

in order to determine the unknown volume.

The unknown volume is attached to the volume measurement device shown in Figure 21, and is evacuated using the vacuum pump. After closing the connecting valve, the measuring tube is filled with ambient air and is balanced easily with the reference system which is also filled with ambient air. Then, the filling valves are closed and the connecting valve is opened to fill the volume being measured with the air above the mercury. The pressure above the mercury is balanced with the reference pressure by filling the measuring tubes with mercury. Temperature is measured with a platinum resistance thermometer attached to a copper block which is in thermal contact with the tubes. Several thermocouples are at different locations along the measuring tubes in order to check the thermal equilibrium of the system.

In this work the unknown volumes were the volumes of the cell, the expansion tanks, and the header which were at different locations in the cryostat and in the oil bath. Their temperatures were also measured with the platinum resistance thermometers which were already mounted on the density measurement apparatus.

The change of the mercury level in the measuring tubes was determined by a Gaertner model 911 cathetometer. During each measurement, it was determined, by means of the cathetometer, whether or not there was any displacement on each tube due to the mercury weight. Measurements for each volume, at room temperature, were repeated several times. The values of the volumes of the test cell were then changed to the temperature of 293.15 K and of the expansion tanks to 300.15 K, which is the constant oil bath temperature, by using the prior results of the thermal expansion test (82).

There is approximately 0.5% difference between the values measured with the volume measuring device by Scott and Sonntag and with the values measured with the modified apparatus in this work. The values obtained with the volume measurement by the method of filling water and weighing it has better agreement (Table XVII).

TABLE XVII

THE VOLUMES OF THE TEST CELL AND THE EXPANSION TANKS

	Cell	Tank I	Tank II
Scott and Sonntag's values:[a] (82)	cc	cc	cc
1) Volume measuring device	75.704	1055.22	1068.60
2) Weight	75.4	1052.5	1063.0
This work with the modified apparatus[b]	74.93	1050.3	1063.3

a) At the temperature of 299.08 K
b) The cell volume at 293.15 K and the volumes of the expansion tanks at 300.15 K.

On the other hand, the volumes of the expansion tanks were checked with the modified Burnett method by Sonntag and Öztürk (88) using both helium and nitrogen. At zero pressure, the ratio of the pressures before and after expansion, approximately 2.0136, is in agreement with the ratio of volumes:

$$\frac{V_2}{V_1} = \frac{V_I+V_{II}+V_H+V_{valves}}{V_I} = \frac{2115.09}{1050.3} = 2.0138.$$

CHAPTER VI

EXPERIMENTAL RESULTS

A. REDUCTION OF DATA

1. General. A computer program whose flow diagram is shown in Figure (23) was made to obtain the corrected PvT data from the raw data collected during the experiment. In this section, the evaluation of all the quantities, corrections, and so forth will be discussed.

All of the temperatures measured with the resistance thermometers which are in the cell and in the oil bath were calculated by linear interpolation from the calibration report supplied by NBS. The resistance thermometer in the oil bath was changed before the experiment of the argon-neon system and the new thermometer was calibrated in the Thermodynamics Laboratory with the former between the temperatures 295 and 305 K. Temperature differences measured with thermocouples were determined by means of large scale sensitivity diagrams (EMF per degree Kelvin against temperature) which were plotted for the copper vs. constantan and the copper vs. gold-cobalt thermocouples.

The compressibilities were determined from the generalized compressibility chart by means of the reduced temperatures and the reduced pressure. The pseudo-critical constants were calculated using Kay's rule.

2. Pressure calculations. The pressures for the test cell were measured by means of the dead weight gage (DWG), and then the hydrostatic pressure correction was made. On the other hand, the tank pressures were measured by the air piston gage (APG).

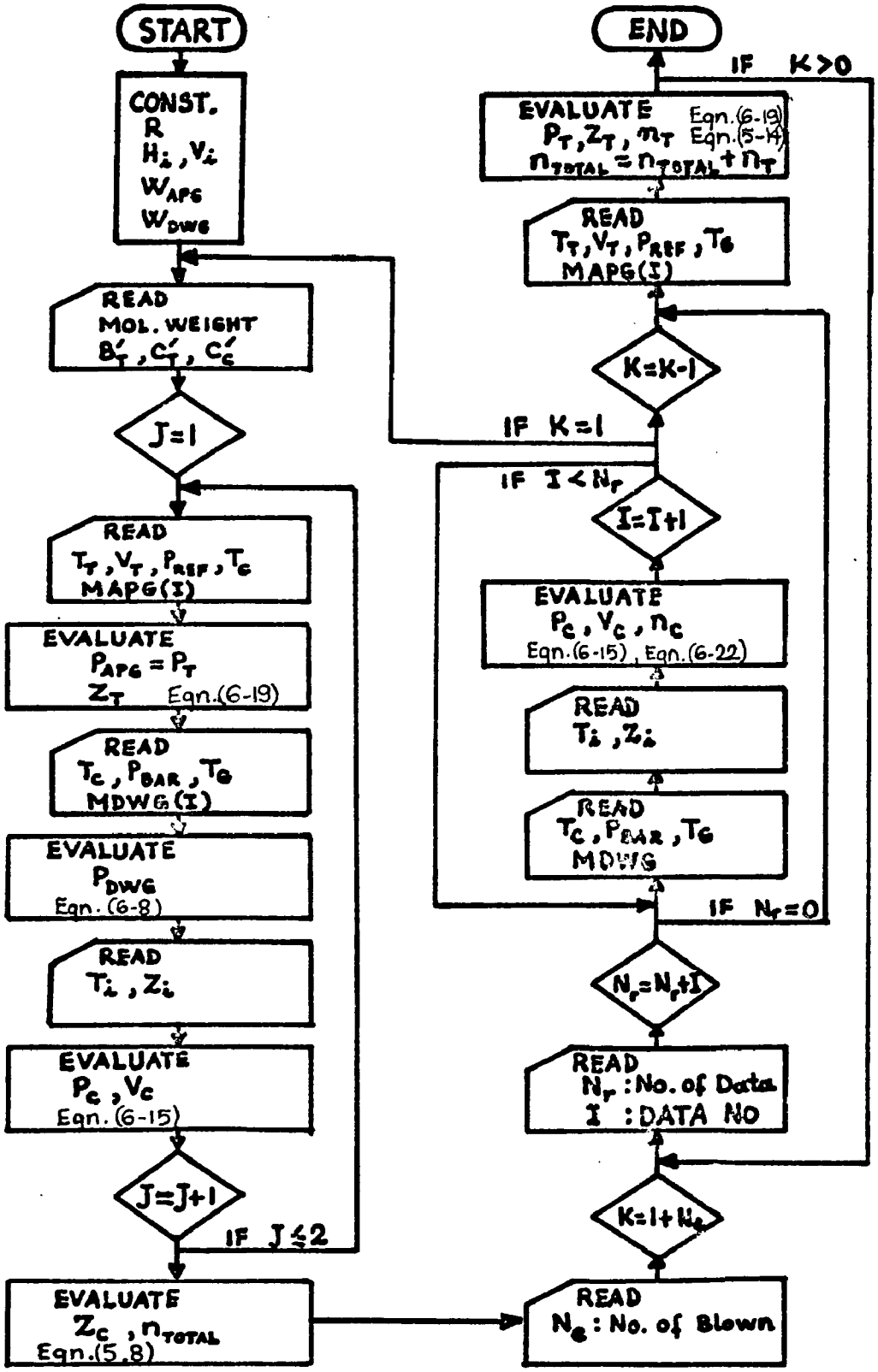


Figure 23. Computer flow diagram for the reduction of experimental data

a) DWG. The pressures measured by the DWG were calculated using the method given by the Ruska Instrument Corporation, as follows,

$$P_{DWG} = P_{BAR} + \frac{TW \times f_1 \times f_2}{A_{nom} \times f_3 \times f_4} + P_{oil} + P_{DPI} \qquad (6\text{-}1)$$

where P_{DWG} is the gage pressure measured by the DWG and P_{BAR} is the ambient pressure measured with the barometer. The temperature correction for the barometric pressure was done by means of the correction-pressure diagram (temperature is a parameter) obtained from the table given by the manufacturer. The gravity correction (g_L/g_S) for the barometric pressure was made in the computer program.

TW (lbf.) is the total weight of the mass used for the pressure measurement which is calculated by means of the standard gravitational acceleration, g_S = 32.174 ft/sec^2, as

$$TW(lbf) = \frac{TM(lbm) \times g_S(ft/sec^2)}{32.174 \ \frac{lbm\text{-}ft}{lbf\text{-}sec^2}} \qquad (6\text{-}2)$$

Therefore, it is necessary to make corrections, f_1, due to the local gravity, as

$$f_1 = \frac{g_L}{g_S} \qquad (6\text{-}3)$$

where g_L is the local gravitational acceleration which has correlated accurately as 980.302 cm/sec^2 for the laboratory's location in Ann Arbor by Scott and Sonntag (82) and g_S is 980.665 cm/sec^2; and f_2 is the buoyancy correction due to the air surrounding the mass which is given by

$$f_2 = 1 - \frac{0.0012}{8.4} \qquad (6\text{-}4)$$

Thus, the true weight of the mass may be obtained.

A_{nom} (in^2) is the nominal area of the piston at the temperature of 25c and 1 atm. pressure, which is given as 0.13022 in^2 for the low range

piston or 0.0260417 in^2 for the high range piston. f_3 and f_4 are the corrections due to thermal expansion and elastic distortion, respectively, which may be calculated by

$$f_3 = 1 + 1.6x10^{-5} (T_g-25) \quad (6\text{-}5a)$$

$$f_4 = 1 + C_4 \cdot P_{nom} \quad (6\text{-}5b)$$

where T_g is the gage temperature in Celsius and C_4 is $-5.4x10^{-8}$ in^2/lbf for the low range piston and C_4 is $-3.6x10^{-8}$ for the high range piston; $P_{nom}(lbf/in^2)=TW/A_{non}$ is the operating pressure.

P_{oil} is the pressure due to the hydrostatic oil head between the reference planes of the DPI and the DWG. The reference planes of the low range and the high range pistons are different and the difference from the fixed reference line which is on the gage is given for each piston in the DWG report. The distance between the reference line on the gage and the reference plane of the DPI has been given as 0.681 cm (0.268 in) (82). Thus, the oil head for the low range and high range pistons are found to be 0.268 in. and 228 in., respectively. Then, P_{oil} may be calculated from

$$P_{oil} = \rho_{oil} \times \frac{g_L}{g_C} h \quad (6\text{-}6)$$

using the density for oil of 0.85 gm/cc. So, P_{oil} is found to be 0.00831 lbf/in^2 for the low range piston and to be 0.00707 lbf/in^2 for the high range piston.

The DPI has a zero shift as a function of pressure, which may be derived as

$$P_{DPI} = 3.56x10^{-6} P_{nom} \quad (6\text{-}7)$$

Consequently, the equation used in the computer program as derived from equation (6-1) is,

$$P_{DWG} = P_{BAR} + \frac{TW \times \frac{g_L}{g_S} \times (1 - \frac{0.0012}{8.4})}{A_{nom}[1+1.6\times10^{-5}(T_g-25)](1+C_4P_{nom})} + P_{oil} + 3.56\times10^{-6}$$

$$+ P_{oil} + 3.56\times10^{-6}P_{nom} \qquad (6\text{-}8)$$

where Pressures: = lbf/in^2

Weight = lbf

Temperature = Celsius

g_L = 980.302 cm/sec^2 (Thermo.Lab., Ann Arbor)

g_S = 980.665 cm/sec^2

	A_{nom} (in^2)	C_4 (in^2/lbf)	P_{oil} (lbf/in^2)
Low range piston	0.13022	-5.4×10^{-8}	0.00831
High range piston	0.0260417	-3.6×10^{-8}	0.00707

b). Hydrostatic pressure correction. In the equipment, as shown in Figure 17, the DPI which is in the constant temperature oil bath is connected to the test cell in the cryostat with a long (0.020 inch inside diameter) stainless steel tube. Along the tube temperature changes from about 300 K to about 100 or 140 K. Even though the pressure difference along the tube is not too large, it is necessary to calculate the cell pressure including the effect of hydrostatic pressure.

The pressure in a fluid changes with the height due to the weight of the fluid and this may be written as

$$dP = -\rho \frac{g_L}{g_C} dh = -\frac{P}{Z(R/M)T} \frac{g_L}{g_C} dh \qquad (6\text{-}9)$$

where ρ, P, Z, T, and M are the density, pressure, compressibility, temperature and molecular weight of the fluid in the tube, while R is the universal gas constant, g_L is the local gravity, and g_C is the conver on

factor. Then the equation (6-9) may be arranged as

$$\frac{dP}{P} = - \frac{g_L}{(R/M)g_C} \cdot \frac{dh}{Z \cdot T} \tag{6-10}$$

Here, the term $g_L/(R/M)g_C$ is constant for a certain fluid and at a certain place. Though the compressibility, Z, is a function of the temperature and the pressure, Z may be assumed to be only a function of temperature because the pressure difference along the tube is negligible. Thus, equation (6-10) may be integrated along the tube as

$$\int_{P_{DWG}}^{P} \frac{dP}{P} = - \frac{g_L}{(R/M)g_C} \int_{o}^{h} \frac{dh}{Z \cdot T} \tag{6-11}$$

Considering the increments, as shown in Figure 17, the integration may be written

$$\ln \frac{P}{P_{DWG}} \cong - \frac{g_L}{(R/M)g_C} \sum_{i=1}^{j} \frac{h_i}{Z_i T_i} \tag{6-12}$$

where h_i's are the height of the segments given in Figure 17. Let us define the hydrostatic pressure correction for the segment i, as

$$\ln f_i = - \frac{g_L}{(R/M)g_C} \frac{(-1)^n h_i}{Z_i \cdot T_i} \tag{6-13}$$

where n=0 for the segments on the side of the DPI and n=1 for the segment on the side of the test cell. Then, the pressure in the segment j is

$$P_j = P_{DWG} \prod_{i=1}^{j} f_i \tag{6-14}$$

and the pressure in the cell is

$$P_C = P_{DWG} \prod_{i=1}^{10} f_i \tag{6-15}$$

c) APG. The pressures measured by the APG were determined in the computer program (Figure 23) with the method given by the Ruska Instrument Corporation as follows,

$$P_{APG} = P_{ref} + \frac{TW}{A_{nom}} (f_1+f_2+f_3) \qquad (6\text{-}16)$$

where P_{APG} is the gage pressure measured with the APG and P_{ref} is the pressure surrounding the weights. It is the ambient pressure for the manual weight loader or it is a vacuum if the vacuum weight loader is used. The ambient pressure is determined by using the barometer, which is calibrated by means of the APG with the vacuum weight loader. Corrections were made for the effects of temperature and local gravity on the barometric pressure readings, as mentioned above in part a (DWG pressure calculation). Vacuum pressure was measured by the vacuum gage which was calibrated using the McLeod gage.

TW (lbf) is the total weight of the apparent mass including the piston which was used for the measurement, and the weight which was calculated under the effect of the standard gravitational acceleration as given by equation (6-2). $A_{nom}(in^2)$ is the piston area at the temperature of 20 C. A_{nom} is 0.0130045 in^2 for the high range piston and is 0.520266 in^2 for the low range piston. Then, f_1, f_2, f_3 are the corrections due to the local gravity (as given in equation (6-3)), due to the buoyancy, and due to the thermal expansion of the piston, respectively.

$$f_2 = -1.0 \times 10^{-5} P_{ref} \qquad (6\text{-}17)$$

$$f_3 = C_3(T_g-20) \qquad (6\text{-}18)$$

where $P_{ref}(lbf/in^2)$ is the same mentioned in equation (6-16),

$C_3 = 1.0 \times 10^{-5}\ K^{-1}$ for the high range piston or $C_3 = -2.0 \times 10^{-5}\ K^{-1}$ for the low range piston and T_g is the gage temperature in degree Celsius.

Thus the equation (6-16) was written for the computer program as follows,

$$P_{APG} = P_{ref} + \frac{TW}{A_{nom}} \left(\frac{g_L}{g_S} - 10^{-5} \times P_{ref} + C_3 \, (T_g - 20) \right) \qquad (6\text{-}19)$$

where,

Pressures: lbf/in^2

Weight: lbf

Temperature: Celsius

g_L = 980.302 cm/sec^2 (Ann Arbor)

g_S = 980.665 cm/sec^2

	A_{nom} (in^2)	C_3 (1/K)
High piston range:	0.0130045	-1.0×10^{-5}
Low piston range:	0.520266	-2.0×10^{-5}

3. Mass Calculation. Recalling equation (5-1), the total number of moles in the system may be found as follows,

$$n_{C1} = \frac{P_{C1} \, V_{C1}}{Z_{C1} R T_{C1}} \qquad (6\text{-}20)$$

where P_{C1}, V_{C1}, T_{C1}, and Z_{C1} are the cell pressure, volume, temperature, and compressibility after the first expansion. The pressure and the compressibility may be determined by equations (6-15) and (5-7) respectively. T_{C1} is correlated as mentioned before. The corrected volume is found by using the following equation,

$$V_C = (1 + \alpha)^3 \ V_{20} \qquad (6\text{-}21)$$

where V_C and V_{20} are the cell volumes at the cell temperature T_C and 293.15 K (Table 18) and $\alpha = (L-L_{20})/L_{20}$ is the thermal strain.

Previously (82), the thermal strain of the cell material had been measured. The results were fitted empirically to the following equation

$$\alpha = -0.00453 + 0.01545 \left(\frac{T_C}{1000}\right) + 0.004\, e^{-24.75\left(\frac{T_C}{1000}\right)} \qquad (6\text{-}22)$$

for temperatures higher than about 70 K. The equation

$$n_{T1} = \frac{P_{T1}\, V_{T1}}{Z_{T1} R\, T_{R1}} \qquad (6\text{-}23)$$

gives the number of moles in the expansion tank. P_{T1} and Z_{T1} are determined by the equations (6-19) and (5-12). The isothermal expansion correction of the tank volumes due to pressure may be estimated from the diagram of the pressure vs. the volume change which is given in reference (82).

The number of moles in the tube, even though very small, should be determined by

$$n_{TUBE\ 1} = \sum_{i=1}^{10} n_{i1} = \sum_{i=1}^{10} \frac{P_{i1} V_i}{Z_{i1} R T_{i1}} \qquad (6\text{-}24)$$

The P_{i1}'s may be calculated by equation (6-14). The V_i's are the volumes of the segments given in Figure 17, and the Z_{i1}'s are estimated from the generalized compressibility chart as mentioned above.

The same calculations may be done after the second expansion and the result, of course, will be the same.

It should be noted that the number of moles in the tube at each data condition is subtracted from the total number of moles in the system in order to determine the specific volume as follows,

$$v_{C_{T,P}} = \frac{v_{C_T}}{n-(\sum n_i)_{T,P}} \qquad (6\text{-}25)$$

4. Composition Determination. Neon-Nitrogen mixtures were prepared in the Thermodynamics Laboratory and the composition of the mixture was determined in the Mass Spectrometer Laboratory of the Chemical and Metallurgical Engineering Department of The University of Michigan. The samples were taken after each expansion into the expansion tank and also at the end of the experiment in order to check whether the composition changed or not during the expansion process. The argon-neon mixture was purchased from the Union Carbide Corporation with the composition analysis report.

The compositions of mixtures are as follows:

1) 45.82% Ar, 53.18% Ne

2) 51.4% Ne, 48.6% N_2

B. CALCULATED EXPERIMENTAL RESULTS

The calculated experimental results, pressure in atmospheres, specific volume in cc/mole, temperature in Kelvin, and compressibility are listed for the argon-neon mixture in Table XVIII and for the neon-nitrogen mixture in Table XIX.

One run was made for each system mentioned above. Two expansion processes were done during each run; in other words, the experimental data were obtained for three different densities. Thus, 13 experimental data points were obtained for the argon-neon system (46.82% Ar, 53.18% Ne) in the temperature range from 115 K to 145 K, at pressures between 20-120 atmospheres, and 12 experimental data points for the neon-nitrogen system (51.4% Ne, 48.6% N_2) in the temperature range from 100 K to 140 K, at pressures between 20-90 atmospheres.

TABLE XVIII

EXPERIMENTAL PvT DATA OF THE ARGON-NEON SYSTEM

46.82% Ar; 53.18% Ne				
Data No.	T K	P atm.	v cc/mole	Z
1511	100.007 sat.	61.299	83.970	0.627
1512	109.209 sat.	69.684	84.001	0.653
1513	119.453 sat.	81.095	84.112	0.696
1514	129.984 sat.	95.585	84.223	0.755
1515	134.848 sat.	102.718	84.279	0.782
1516	140.109	111.140	84.353	0.815
1517	144.897	118.062	84.403	0.838
1523	125.314 sat.	57.257	140.916	0.785
1524	129.946	61.973	141.050	0.820
1525	134.817	65.697	141.107	0.838
1526	139.706	69.406	141.214	0.855
1527	144.888	73.281	141.296	0.871
1530	110.000 sat.	20.013	362.884	0.805
1531	114.991	23.020	363.884	0.886
1532	119.955	24.361	363.491	0.900
1533	124.971	25.637	363.684	0.909
1534	129.960	26.895	363.805	0.917
1535	134.911	28.140	364.042	0.925
1536	139.894	29.389	364.226	0.932
1537	144.862	30.622	364.427	0.939

TABLE XIX

EXPERIMENTAL PvT DATA OF THE NEON-NITROGEN SYSTEM

51.4% Ne; 48.6% N_2				
Data No.	T K	P atm.	v cc/mole	Z
1411	79.996 sat.	31.070	114.978	0.544
1412	90.002 sat.	37.215	114.950	0.579
1413	100.031 sat.	45.352	114.942	0.635
1414	109.983 sat.	55.056	115.060	0.702
1415	119.993	66.638	115.226	0.780
1416	129.999	76.738	115.374	0.830
1417	139.998	86.688	115.525	0.872
1421	79.989 sat.	17.269	210.810	0.555
1422	89.998 sat.	21.382	210.994	0.611
1423	100.000 sat.	27.778	211.276	0.715
1424	109.999	34.908	211.593	0.818
1425	119.999	39.745	211.828	0.855
1426	129.999	44.490	212.079	0.884
1427	139.994	49.174	212.325	0.909
1431	80.004 sat.	9.667	401.354	0.591
1432	90.008 sat.	12.916	401.857	0.703
1433	100.007	17.738	402.615	0.870
1444	110.004	20.069	402.989	0.896
1455	119.996	22.356	403.387	0.916
1466	130.005	24.620	403.838	0.932
1477	140.000	26.863	404.278	0.945

The pressure-temperature and the compressibility-pressure plots are shown in Figures 24, 25, and 26. The dew-point line for the neon-nitrogen system was estimated from Streett's data (94); however, the argon-neon system was plotted approximately.

C. ERROR ANALYSIS

1. General. Since the same equipment was used previously (82), the details of the uncertainties for each gage is not given unless there is significant difference between the two error analyses.

It should be noted that (R) and (S) in the equations will refer to random and systematic errors, respectively.

2. Temperature. The temperatures of the thermometers in the cell and in the oil bath were read to within $\pm$0.001 K with the Mueller Bridge. Thermodynamic equilibrium was maintained at each data point for approximately one minute. However, an uncertainty of about $\pm$0.001 K due to thermal lag was assumed for the cell temperature. Thus the uncertainty of the cell temperature is $\pm$0.002 K (R).

The oil bath temperature was controlled at 300.15 $\pm$0.01 K by a mercury thermostat. The time-period was about 6-7 minutes. Usually, during the first and second expansions and the expansion processes two measurements were made at the maximum and the minimum values of the oil bath temperature. Therefore, an uncertainty of about $\pm$0.003 K was added for the thermal lag and for the error due to the change of the tank temperature. Thus, the uncertainty for the expansion tanks was assumed to be $\pm$0.004 K(R)

The temperature uncertainty for the thermocouples along the tubes is not really important because of the extremely small volumes of the segments.

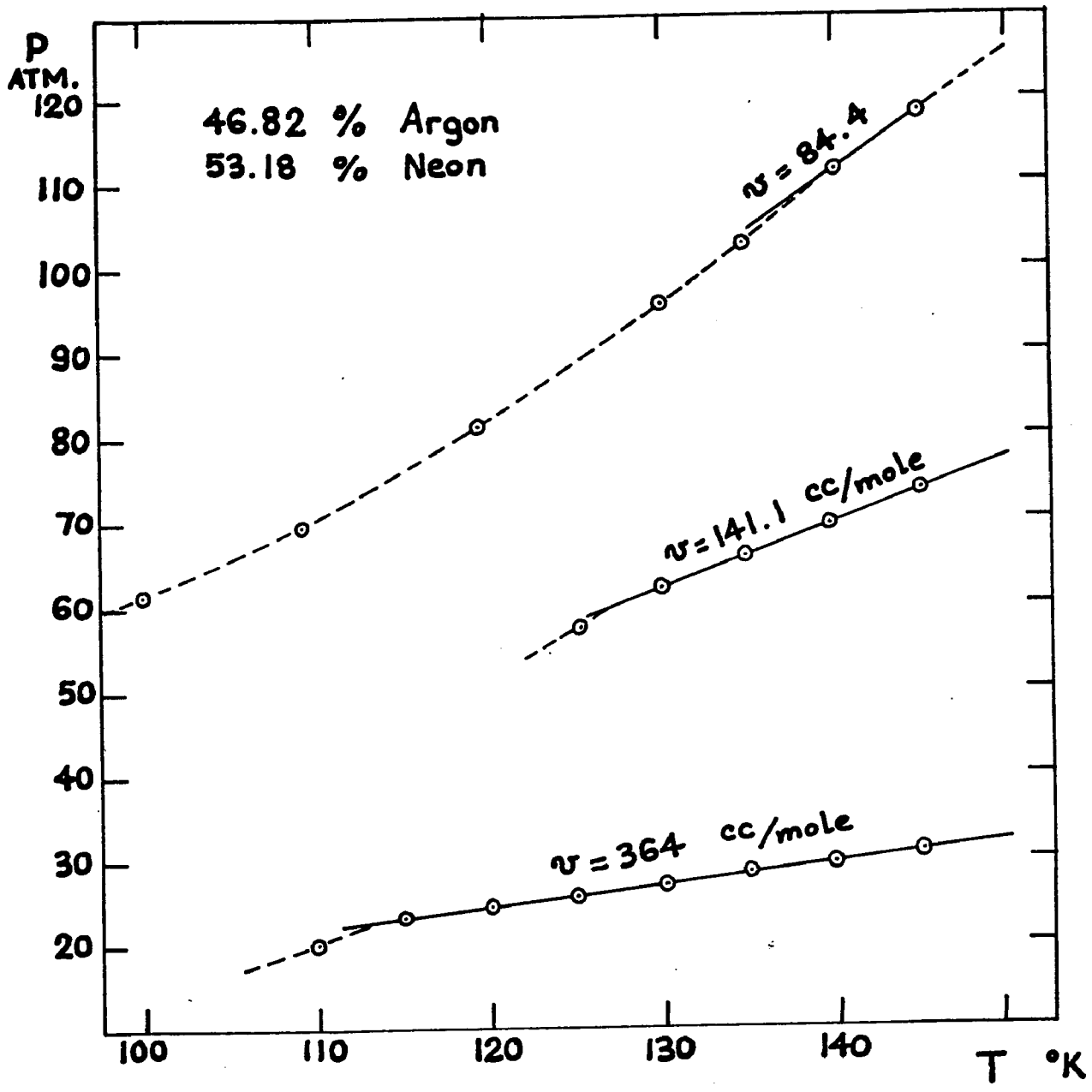


Figure 24. Pressure - temperature plot of the experimental data of the argon-neon mixture.

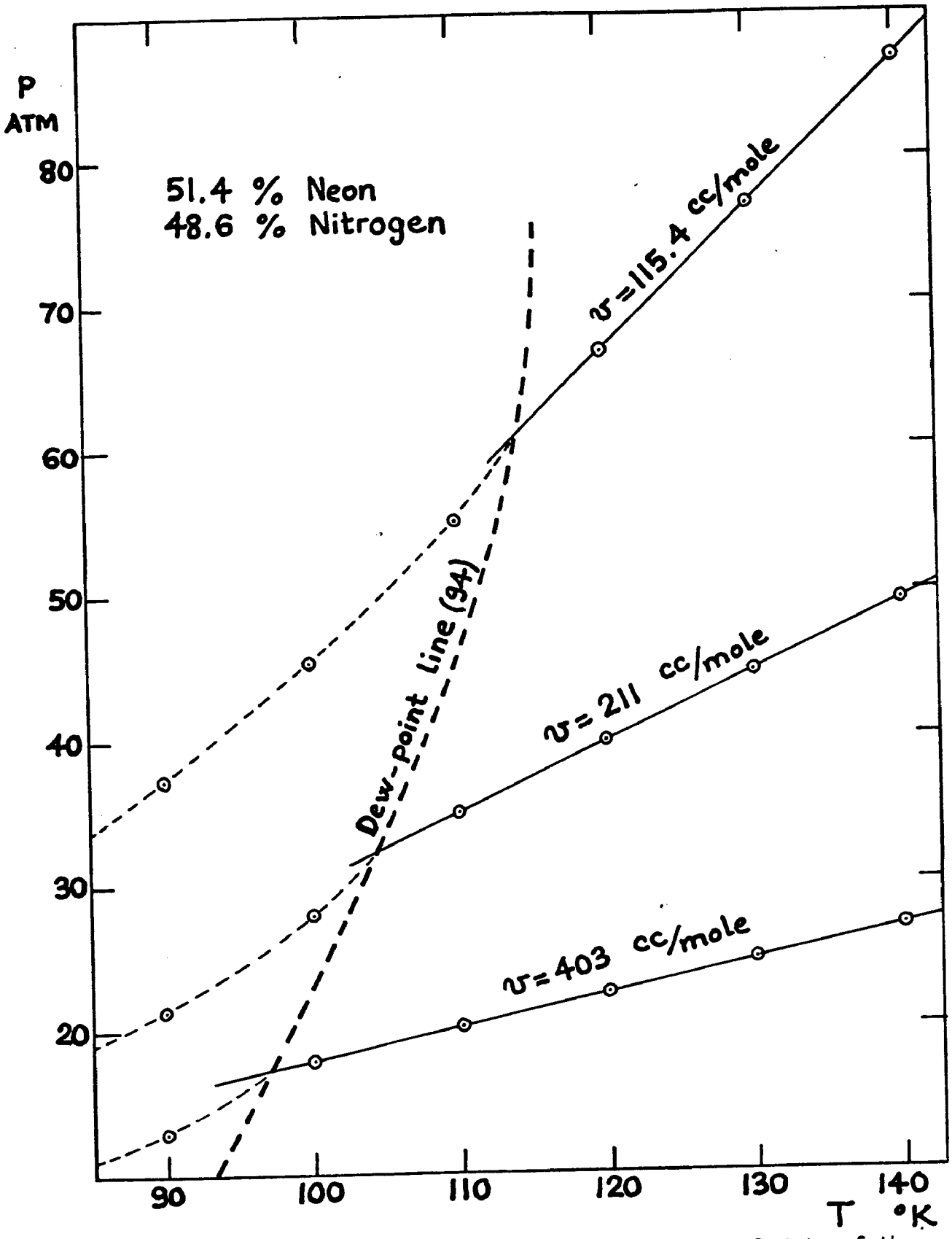
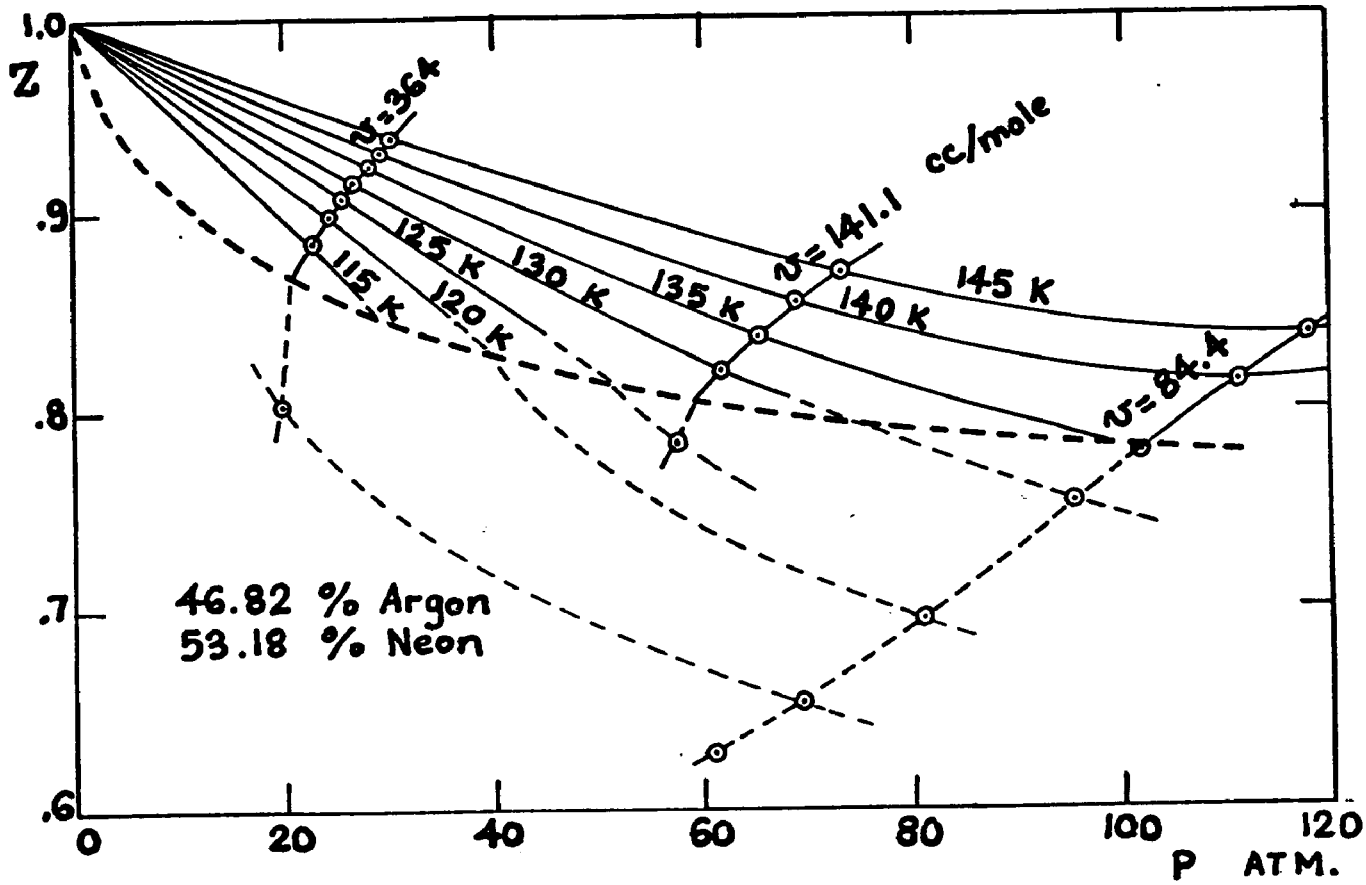


Figure 25. Pressure-temperature plot of the experimental data of the neon-nitrogen mixture.



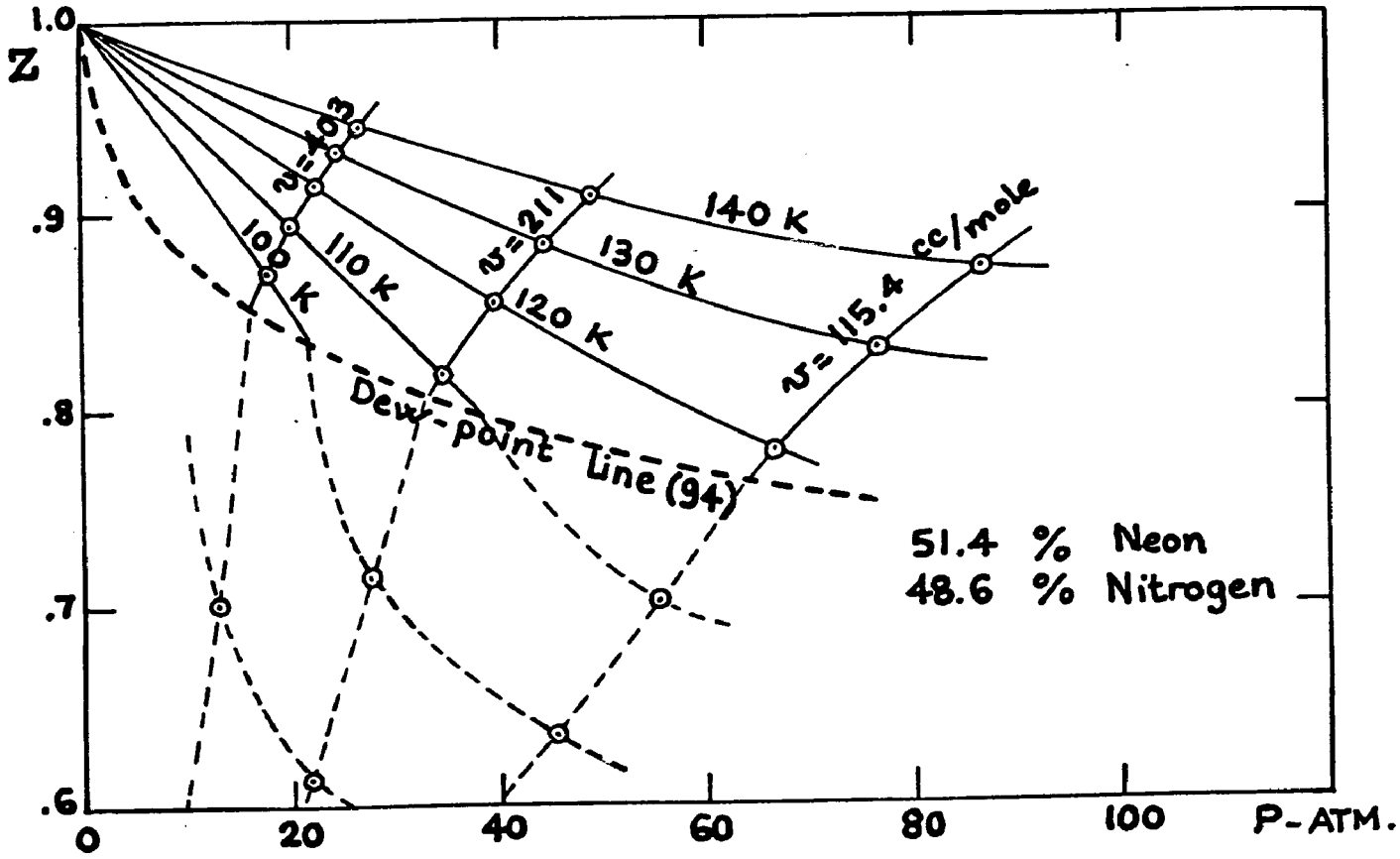


Figure 26. Compressibility-pressure plot of the experimental data.

3. Pressure.

a) DWG. The uncertainty of the pressure measurement with the DWG may be found from the equation derived from equation (6-1), as follows,

$$\Delta P_{DWG} = \Delta P_{BAR} + [\frac{\Delta(TW)}{TW} + \frac{\Delta A}{A_{nom}}]P_{nom} + \Delta P_{oil} + \Delta P_{DWG} \qquad (6.26)$$

where Δ designates the uncertainty of each quantity.

The barometer has an uncertainty of ± 0.001 psi (R) because of its reading with the vernier attachment to ± 0.05 mm. of mercury level.

The resolution which is given in the test report of the DWG is less than 5 ppm. This gives an uncertainty for the total weight as $\pm 5 \times 10^{-6} \times (TW)$. The value of the local gravitational acceleration is uncertain to about ± 0.002 cm/sec^2 and this produces $\pm 2 \times 10^{-4}$ percent systematic error on the total weight. Considering the smallest mass, 0.00013 lbm, which was used during the measurement, the error in pressure due to the mass uncertainty may be evaluated as,

$$\frac{\Delta(TW)}{TW} P_{nom} \cong \begin{matrix} \pm 0.001 \text{ psi(R) (LRP)} \\ \pm 0.005 \text{ psi(R) (HRP)} \end{matrix} \pm 0.7 \times 10^{-5} \; P_{nom}(S) \qquad (6.27)$$

where pressures are in psi, and (LRP) and (HRP) designate the low range and the high range pistons.

The error contributed from the piston area is

$$\frac{\Delta A}{A_{nom}} = \frac{\Delta A_{nom}}{A_{nom}} + 1.6 \times 10^{-5} \; \Delta(\Delta T) + C_4 \cdot \Delta P \qquad (6.28)$$

which is derived from $A_{nom} \times f_3 \times f_4$, substituting equations (6.5) and (6.6). As given in the test report by NBS the piston area of the DWG has an uncertainty of 100 ppm, then $\Delta A_{nom}/A_o = \pm 10 \times 10^{-5}(S)$. The gage temperature is read from a glass mercury thermometer with 1 K division, so $\Delta(\Delta T) = \pm 0.5$ K(R). Because $C_4 \cong 5 \times 10^{-8}$ in^2/lbf. is quite small, the second

term may be neglected and then equation (6.28) yields,

$$\frac{\Delta A}{A_{nom}} = \pm 0.8\times10^{-5}(R)\ \pm 10\times10^{-5}(S) \qquad (6.29)$$

The uncertainties in pressure due to the oil head and due to the DPI shift are ± 0.002 psi (S) and $\pm 5\times10^{-5}$ psi (negligible), respectively.

Consequently, substituting those uncertainties (due to the barometer reading and the oil head correction) and equations (6.27) and (6.29) into equation (6.26), the total uncertainty in pressure measurements with the DWG is:

$$\Delta P_{DWG}(psi) = \begin{bmatrix} \pm 0.002(R)(LRP) \\ \pm 0.006(R)(HRP) \end{bmatrix} \pm 0.002(S) + (\pm 0.8\times10^{-5}(R)\ \pm 10.7\times10^{-5}(S)) \cdot P_{nom}(psi) \qquad (6.30a)$$

$$\Delta P_{DWG}(atm) = \begin{bmatrix} \pm 0.00014(R)(LRP) \\ \pm 0.00040(R)\ (HRP) \end{bmatrix} \pm 0.00014(S) + (\pm 0.8\times10^{-5}(R)\ \pm 10.7\times10^{-5}(S)\ ) \cdot P_{nom}(atm) \qquad (6.30b)$$

b) APG. The uncertainty of the pressure measurement with the air piston gage may be calculated by the equation as follows,

$$\Delta P_{APG} = \Delta P_{ref} + \left[\frac{\Delta(TW)}{TW} + \frac{\Delta A_{nom}}{A_{nom}} + \frac{\Delta g_L}{g_L} + 10^{-5} \cdot \Delta P_{ref} + C_3 \cdot \Delta(\Delta T)\right] P_{nom} \qquad (6.31)$$

which is derived from equation (6.19). Here

$$\Delta P_{ref} = \pm 0.001 \text{ psi (R)} \quad \text{(barometer reading)}$$

$$\frac{\Delta(TW)}{TW} \cdot P_{nom} = \begin{bmatrix} \pm 0.001 \text{ psi (R) (HRP)} \\ \pm 0.001 \text{ psi (R) (LRP)} \end{bmatrix} \pm 1\times10^{-5} \cdot P_{nom}\ (S)$$

$$\frac{\Delta A_{nom}}{A_{nom}} \approx 0.0 \quad \text{(is not reported)}$$

$$\frac{\Delta g_L}{g_L} = \pm 0.2\times10^{-5}(S)$$

$$10^{-5} \cdot \Delta P_{ref} = \pm 10^{-8} \text{ psi (negligible)}$$

$$C_3 \cdot \Delta(\Delta T) = 2\times10^{-5}\times(\pm 0.5) = \pm 1\times10^{-5}(R)$$

Thus, equation (6.31) produces,

$$\Delta P_{APG}(psi) = \begin{bmatrix}\pm 0.002 \ (R) \ (HRP) \\ \pm 0.001 \ (R) \ (LRP)\end{bmatrix} + (\pm 1\times10^{-5}(R) \pm 1.2\times10^{-5}(S)) \cdot P_{nom}(psi) \tag{6.32a}$$

$$\Delta P_{APG}(atm) = \begin{bmatrix}\pm 0.00014 \ (R) \ (HRP) \\ \pm 0.00007 \ (R) \ (LRP)\end{bmatrix} + (\pm 1\times10^{-5}(R) \pm 1.2\times10^{-5}(S)) \cdot P_{nom}(atm) \tag{6.32b}$$

4. Volume. From equation (5.22), the possible uncertainty on the volume measurement is

$$\Delta V_U = \Delta V_M + \frac{\Delta T_U + \Delta T_2}{T_2} \cdot V_M \tag{6.33}$$

or

$$\frac{\Delta V_U}{V_U} \cong \frac{\Delta V_M}{V_M} + \frac{\Delta T_U + \Delta T_2}{T_2} \tag{6.33a}$$

where

$$\Delta V_M = \Delta A \cdot L + A \cdot \Delta L \tag{6.34}$$

or

$$\frac{\Delta V_M}{V_M} = \frac{\Delta A}{A} + \frac{\Delta L}{L} \tag{6.34a}$$

The diametrical tolerance of the high precision bore tubes is $\pm$ 0.0002 in. = $\pm$0.0005 cm. Then,

$$\frac{\Delta A}{A} = 2 \cdot \frac{\Delta D}{D} = \begin{matrix}\pm 0.0004 \\ \pm 0.0011\end{matrix} (S) \begin{matrix}\text{for 1" diameter tube} \\ \text{for 3/8" diameter tube}\end{matrix} \tag{6.35}$$

The change of height of the mercury and the reference point shift were determined with a cathetometer with an error of $\pm$0.005 cm. at each reading. Because of four readings for the measurement of the tank volumes, and two readings for the cell volume and other volumes,

$$\Delta L = \begin{matrix} \pm 0.02 \text{ cm. (R)} & \text{(for the tank volumes)} \\ \pm 0.01 \text{ cm. (R)} & \text{(for the cell and other small volumes)} \end{matrix} \tag{6.36}$$

is obtained. The change of the mercury level is 15 cm. in one tube for the cell volume, 70 cm. in three tubes for the tank volumes, and about 2 cm. in one tube for the header and lead tube volumes. Therefore, the equation (6.34a) yields,

$$\frac{\Delta V_M}{V_M}\text{(TANK)} = \pm 0.0003 \text{ (R)} \pm 0.0012 \text{ (S)}$$

$$\frac{\Delta V_M}{V_M}\text{(CELL)} = \pm 0.0007 \text{ (R)} \pm 0.0004 \text{ (S)}$$

$$\frac{\Delta V_M}{V_M}\text{(TUBES)} = \pm 0.0050 \text{ (R)} \pm 0.0004 \text{ (S)} \tag{6.37}$$

On the other hand, the uncertainties of temperatures is mentioned in part C.2: $\Delta T = \pm 0.002$ K (R) for the cell and $\Delta T = \pm 0.004$ K (R) for the tanks. $\Delta T = \pm 0.004$ K(R) may be assumed for the uncertainty of the measuring tubes temperature. All volume measurements were done at room temperature which is approximately 300 K. Thus,

$$\frac{\Delta T_U + \Delta T_2}{T_2} = \pm \frac{0.008}{300} = \pm 3\times10^{-5} \text{ (R)} \tag{6.38}$$

which may be neglected by comparing it with the values of $\Delta V_M/V_M$ in equation (6.33a); the absolute errors in volume measurement are ± 0.08 cc. for the test cell, ± 1.5 cc. for the tanks and ± 0.008 cc. for the header.

5. Compressibility.

a) Tank. The values of the second and third virial coefficients used for the mass calculation of each system are listed in Table XVI). The pressure in the tank during the expansion process is between about 2 and 5 atm. Recalling equations (5-12) or (5-13), the numerical contributions of each term to the compressibility factor may be calculated as follows;

For the argon-neon system,

$$\begin{aligned} P_1 &= 5 \text{ atm.} \quad ; \quad Z = 1 + 0.00110 + 0.000018 + \ldots \\ P_2 &= 2 \text{ atm.} \quad ; \quad Z = 1 + 0.00044 + 0.000003 + \ldots \end{aligned} \tag{6-39}$$

For the neon-nitrogen system,

$$\begin{aligned} P_1 &= 5 \text{ atm.} \quad ; \quad Z = 1 + 0.00180 + 0.000023 + \ldots \\ P_2 &= 2 \text{ atm.} \quad ; \quad Z = 1 + 0.00072 + 0.000004 + \ldots \end{aligned} \tag{6-40}$$

Now, considering the total differential of the equation (5-12) or (5-13), such as

$$\Delta Z = \left(\frac{\Delta B'}{B'} + \frac{\Delta P}{P}\right) B'P + \left(\frac{\Delta C'}{C'} + 2\,\frac{\Delta P}{P}\right) C'P^2 \tag{6-41}$$

the possible error may be estimated.

From the equation (6-32b) $\Delta P/P$ is found that

$$\frac{\Delta P_1}{P_1} \approx \pm 6 \times 10^{-5} , \qquad \frac{\Delta P_2}{P_2} \approx \pm\, 9 \times 10^{-5}$$

which may be neglected with respect to $\Delta B'/B'$ and equation (6-41) yields

$$Z \approx \Delta B' \cdot P + \Delta C' \cdot P^2 \approx \Delta B' \cdot P \tag{6-42}$$

In reference (16) an error of ± 0.1 cc/mole was estimated for the excess second virial coefficient which is defined as $E = B_{12} - 1/2\,(B_1 + B_2)$. If the error of the second virial coefficients of the pure components are

to be assumed $\pm$0.1 cc/mole the same order of magnitude, ΔB_{12} will be $\pm$ 0.3 cc/mole. Then,

$$\Delta B_m \cong y_1^2 \cdot \Delta B_{11} + 2y_1y_2 \cdot \Delta B_{12} + y_2^2 \cdot \Delta B_{22} \qquad (6\text{-}43)$$

gives the error of the second virial coefficient of the mixtures by ngglecting the uncertainties of the composition which are less than $\pm$ 0.001. $\Delta B_m = \pm 0.2$ cc/mole $\Delta B_m' = \pm 2\times10^{-5}$ 1/atm. are obtained. Substituting the latter value into equation (6-42) $\Delta Z_{T1} = \pm 10\times10^{-5}$ (S) and $\Delta Z_{T2} = \pm 4\times10^{-5}$ (S) may be concluded as the errors for the compressibility factor of the expansion tanks.

b) Test Cell. Differentiating the equation (5-8), the error of the compressibility of the test cell is obtained as,

$$\Delta Z_{C2} \approx \left[1 + \frac{\alpha_1}{(\alpha_1^2 - \alpha_2)^{1/2}}\right] \Delta\alpha_1 - \frac{\Delta\alpha_2}{2(\alpha_1^2 - \alpha_2)^{1/2}} \qquad (6\text{-}44)$$

Here $\Delta\alpha_1$, $\Delta\alpha_2$ are derived from the equations (5-9) and (5-10) as follows

$$\Delta\alpha_1 \approx \frac{1}{2}\frac{P_{C2}}{P_{C1}}\left(\frac{\Delta P_{C1}}{P_{C1}} - \frac{\Delta P_{C2}}{P_{C2}}\right) \qquad (6\text{-}44a)$$

$$\Delta\alpha_2 \approx \frac{P_{C2}V_{C2}}{\delta T_{C2}}\left(1 - \frac{P_{C2}}{P_{C1}}\right)\left(\frac{\Delta P_{C1}}{P_{C1}} + \frac{\Delta V_{C2}}{V_{C2}} + \frac{\Delta T_{C2}}{T_{C2}} + \frac{\Delta\delta}{\delta}\right) \qquad (6\text{-}44b)$$

where

$$\frac{\Delta\delta}{\delta} \approx \frac{\Delta P_{T1}}{P_{T1}} + \frac{\Delta V_{T1}}{V_{T1}} + \frac{\Delta Z_{T1}}{Z_{T1}} + \frac{\Delta T_{T1}}{T_{T1}} - \left(\frac{\Delta P_{T2}}{P_{T2}} + \frac{\Delta V_{T2}}{V_{T2}} + \frac{\Delta Z_{T2}}{Z_{T2}} + \frac{\Delta T_{T2}}{T_{T2}}\right) \qquad (6\text{-}44c)$$

It may be calculated approximately that $\alpha_1 \approx 0.25$, $(\alpha_1^2 - \alpha_2)^{1/2} \approx 0.75$, $P_{C2}/P_{C1} \approx 0.5$ and $P_{C2} \cdot V_{C2}/\delta \cdot T_{C2} \approx -1$. Substituting these values into equations (6-44), (6-44a), and (6-44b)

$$\Delta Z_{C2} \approx \frac{4}{3} \cdot \Delta\alpha_1 - \frac{2}{3} \cdot \Delta\alpha_2 \qquad (6\text{-}45)$$

$$\Delta\alpha_1 \approx \frac{1}{4}\left(\frac{\Delta P_{C1}}{P_{C1}} - \frac{\Delta P_{C2}}{P_{C2}}\right) \qquad (6\text{-}45a)$$

$$\Delta\alpha_2 \approx -\frac{1}{2}\left(\frac{\Delta P_{C1}}{P_{C1}} + \frac{\Delta V_{C2}}{V_{C2}} + \frac{\Delta T_{C2}}{T_{C2}} + \frac{\Delta\delta}{\delta}\right) \qquad (6\text{-}45b)$$

are obtained. The random and systematic errors on the pressure, temperature, volume, and compressibility at the approximate state of the expansion processes are listed in the Table XX.

It is evident that the systematic errors on the properties measured with the same gage will cancel each other if they have different signs in the equations written above.

Thus, the equations (6-44c), (6-45a), and (6-45b) produce the following results:

$$\frac{\Delta\delta}{\delta} = \pm 7.7\times10^{-4}(R)\ \pm0.6\times10^{-4}(S) \qquad (6\text{-}46a)$$

$$\Delta\alpha_1 = \pm0.8\times10^{-4}(R)\ \ \pm0.1\times10^{-4}(S) \qquad (6\text{-}46b)$$

$$\Delta\alpha_2 = \pm8.2\times10^{-4}(R)\ \ \pm2.5\times10^{-4}(S) \qquad (6\text{-}46c)$$

On the other hand, substituting equations (6-44c), (6-45a), and (6-45b) into equation (6-45) and using the values given in Table (6-3),

$$\Delta Z_{C2} = \pm6.5\times10^{-4}(R)\ ^{+}\text{-}1.8\times10^{-4}(S) \qquad (6\text{-}47)$$

is estimated.

TABLE XX

RANDOM AND SYSTEMATIC ERRORS DURING

THE MASS DETERMINATION PROCESS

	TEST CELL ($T \approx 140$ K)			
	$P_1 \approx 4$-5 atm.		$P_2 \approx 2$-2.5 atm.	
	Random	Systematic	Random	Systematic
$\frac{\Delta P}{P}$	$\pm 1.4 \times 10^{-4}$	$\pm 0.4 \times 10^{-4}$	$\pm 1.8 \times 10^{-4}$	$\pm 0.8 \times 10^{-4}$
$\frac{\Delta V}{V}$	$\pm 7.0 \times 10^{-4}$	$\pm 4.0 \times 10^{-4}$	$\pm 7.0 \times 10^{-4}$	$\pm 4.0 \times 10^{-4}$
$\frac{\Delta T}{T}$	$\pm 0.2 \times 10^{-4}$		$\pm 0.2 \times 10^{-4}$	
	EXPANSION TANKS ($T \approx 300$ K)			
	$P_1 \approx 4$-5 atm.		$P_2 \approx 2$-2.5 atm.	
	Random	Systematic	Random	Systematic
$\frac{\Delta P}{P}$	$\pm 0.5 \times 10^{-4}$	$\pm 0.1 \times 10^{-4}$	$\pm 0.8 \times 10^{-4}$	$\pm 0.1 \times 10^{-4}$
$\frac{\Delta V}{V}$	$\pm 3.0 \times 10^{-4}$	$\pm 12.0 \times 10^{-4}$	$\pm 3.0 \times 10^{-4}$	$\pm 12.0 \times 10^{-4}$
$\frac{\Delta T}{T}$	$\pm 0.2 \times 10^{-4}$		$\pm 0.2 \times 10^{-4}$	
$\frac{\Delta Z}{Z}$		$\pm 1.0 \times 10^{-4}$		$\pm 0.4 \times 10^{-4}$

Using the following equation, which is derived from equation (5-7),

$$\Delta Z_{C1} = \frac{P_{C1}}{P_{C3}} (Z_{C2}-1) \left(\frac{\Delta P_{C1}}{P_{C1}} + \frac{\Delta P_{C2}}{P_{C2}} + \frac{\Delta Z_{C2}}{Z_{C2}}\right) \qquad (6\text{-}48)$$

ΔZ_{C1} may be calculated as $\pm 3.4 \times 10^{-4}$ (R) $\pm 1.2 \times 10^{-4}$ (S).

6. Mass Calculation.

$$\frac{\Delta n_{C1}}{n_{C1}} = \left(\frac{\Delta P_{C1}}{P_{C1}} + \frac{\Delta V_{C1}}{V_{C1}} + \frac{\Delta Z_{C1}}{Z_{C1}} + \frac{\Delta T_{C1}}{T_{C1}}\right) \quad (6\text{-}49)$$

$$\frac{\Delta n_{T1}}{n_{T1}} = \left(\frac{\Delta P_{T1}}{P_{T1}} + \frac{\Delta V_{T1}}{V_{T1}} + \frac{\Delta Z_{T1}}{Z_{T1}} + \frac{\Delta T_{T1}}{T_{T1}}\right) \quad (6\text{-}50)$$

are produced from equations (6-20) and (6-21). Then

$$\frac{\Delta n_{C1}}{n_{C1}} = \pm 12.0\times10^{-4}(R) \pm 5.6\times10^{-4}\ (S)$$

$$\frac{\Delta n_{T1}}{n_{T1}} = \pm 3.7\times10^{-4}\ (R) \pm 13.1\times10^{-4}(S)$$

are obtained. In the same manner

$$\frac{\Delta n_{C2}}{n_{C2}} = \pm 15.5\times10^{-4}\ (R) \pm 6.6\times10^{-4}\ (S)$$

$$\frac{\Delta n_{T2}}{n_{T2}} = \pm 4.0\times10^{-4}\ (R) \pm 12.5\times10^{-4}\ (S)$$

On the other hand, from equation (5-1)

$$\frac{\Delta n}{n} = \frac{n_{C1}}{n}\left(\frac{\Delta n_{C1}}{n_{C1}}\right) + \frac{n_{T1}}{n}\left(\frac{\Delta n_{T1}}{n_{T1}}\right) = \frac{n_{C2}}{n}\left(\frac{\Delta n_{C2}}{n_{C2}}\right) + \frac{n_{T2}}{n}\left(\frac{\Delta n_{T2}}{n_{T2}}\right) \quad (6\text{-}51)$$

may be derived. Although the uncertainties of the number of moles in the cell are larger than in the tanks, the ratio of the number of moles in the cell to the total number of moles is smaller, as

$$\frac{n_{C1}}{n} = \frac{V_{C1}}{\frac{T_{C1}}{T_{T1}} V_{T1} + V_{C1}} \approx 0.13 \quad (6\text{-}52)$$

$$\frac{n_{C2}}{n} = \frac{V_{C2}}{\frac{T_{C2}}{T_{T2}} V_{T2} + V_{C2}} \approx 0.07 \quad (6\text{-}53)$$

Then equation (6-51) yields the uncertainty of the total number of moles as

$$\frac{\Delta n}{n} = \pm 4.8\times10^{-4}(R) \pm 12.1\times10^{-4}(S) = \pm 0.17\%$$

The uncertainty of the number of moles which are blown into the expansion tank or tanks are the same uncertainty obtained for the tank from equation (6-50) which is about $\pm 0.17\%$. This means that the error on the mass determination never exceeds $\pm 0.17\%$.

The uncertainty of the specific volume can be found now as follows,

$$\frac{\Delta v}{v} = \frac{\Delta n}{n} - \frac{\Delta V_c}{V_c} \qquad (6\text{-}54)$$

The errors on the total number of moles in the system and on the cell volume are rather large; however, the systematic errors due to volume measurements, and also the random errors due to the cell volume measurement cancel each other. Thus, the equation (6-54) yields,

$$\frac{\Delta v}{v} = \pm 10.8\times10^{-4}(R) \pm 8.2\times10^{-4}(S) = \pm 0.19\%$$

It is necessary to say that all of these uncertainties are maximum but not probable.

CHAPTER VII

CONCLUSIONS

A. GENERAL

The constants of the equation of state studied in this work, which was mainly concerned with mixtures, were determined for argon, neon, and nitrogen (Table XV-1,2) from the general behavior of substances. In the selection of the equation of state and the technique used for obtaining the constants of pure components it was essentially considered that, if a generalized equation and a generalized approach to determine the constants were utilized, the corresponding constants might have more consistency in the equation than in other empirical equations of state.

Under these circumstances, the equation has been applied to the mixtures with a new combining rule and tested primarily with the argon-nitrogen system and partially with the argon-neon and neon-nitrogen systems. As known, it is difficult to represent the overall PvT surface of a pure substance with a single equation and more difficult with a single set of constants. Therefore it is evident that to represent the PvT behavior of a mixture is much more difficult because it not only depends on the equation of state, but also depends on the combining rules and the constants of the pure components. On the other hand the mixtures, especially in the critical region, behave quite differently than the pure substances (Chapter III, Part B.1).

The combining rule which has been derived essentially from the corresponding state theory is quite simple. The pseudo-critical constants have been correlated by means of basic combining rules.

In order to compare the calculated results with the experimental data and the other more accurate equations, the PvT surface has been

divided into different regions, as shown in Figure 27, according to temperatures, specific volumes, and pressures, as follows:

$$\text{I} \quad : \quad T_r < 1 \quad , \quad 1 < v_r$$

$$\text{IIa} \quad : \quad T_r > 1 \quad , \quad 1 < v_r \quad , \quad P_r < 1$$

$$\text{IIb} \quad : \quad T_r > 1 \quad , \quad 1 < v_r \quad , \quad P_r > 1$$

$$\text{IIIa} \quad : \quad T_r > 1 \quad , \quad \frac{1}{1.5} < v_r < 1$$

$$\text{IIIb} \quad : \quad T_r > 1 \quad , \quad \frac{1}{1.8} < v_r < \frac{1}{1.5}$$

$$\text{IIIc} \quad : \quad T_r > 1 \quad , \quad \frac{1}{2.0} < v_r < \frac{1}{1.8}$$

$$\text{IV} \quad : \quad T_r < 1 \quad , \quad v_r < 1$$

Appendices I.1,2,3 for pure components argon, neon, and nitrogen and Appendices II.1,2,3 for argon-nitrogen (three different compositions), argon-neon, and neon-nitrogen systems show experimental PvT data in atmospheres, cc/mole, and Kelvin with their sources, calculated pressures at the same temperature and specific volume of the experimental data, experimental and calculated compressibility using $R=82.0597\frac{\text{atm.cc}}{\text{mole-K}}$ and Dev. % defined by equation (4-14) as

$$\text{Dev. \%} = \frac{P_{cal}-P_{exp}}{P_{exp}} \times 100 = \frac{Z_{cal}-Z_{exp}}{Z_{exp}} \quad 100$$

In the appendices, the percentage deviation of the other equations, which may be accepted as the best equation for that particular substance, is given. In each region, the average percentage deviations of both equations (Avg. Dev. %), which is the average of the absolute values of the individual percentage deviations, is also given for comparison.

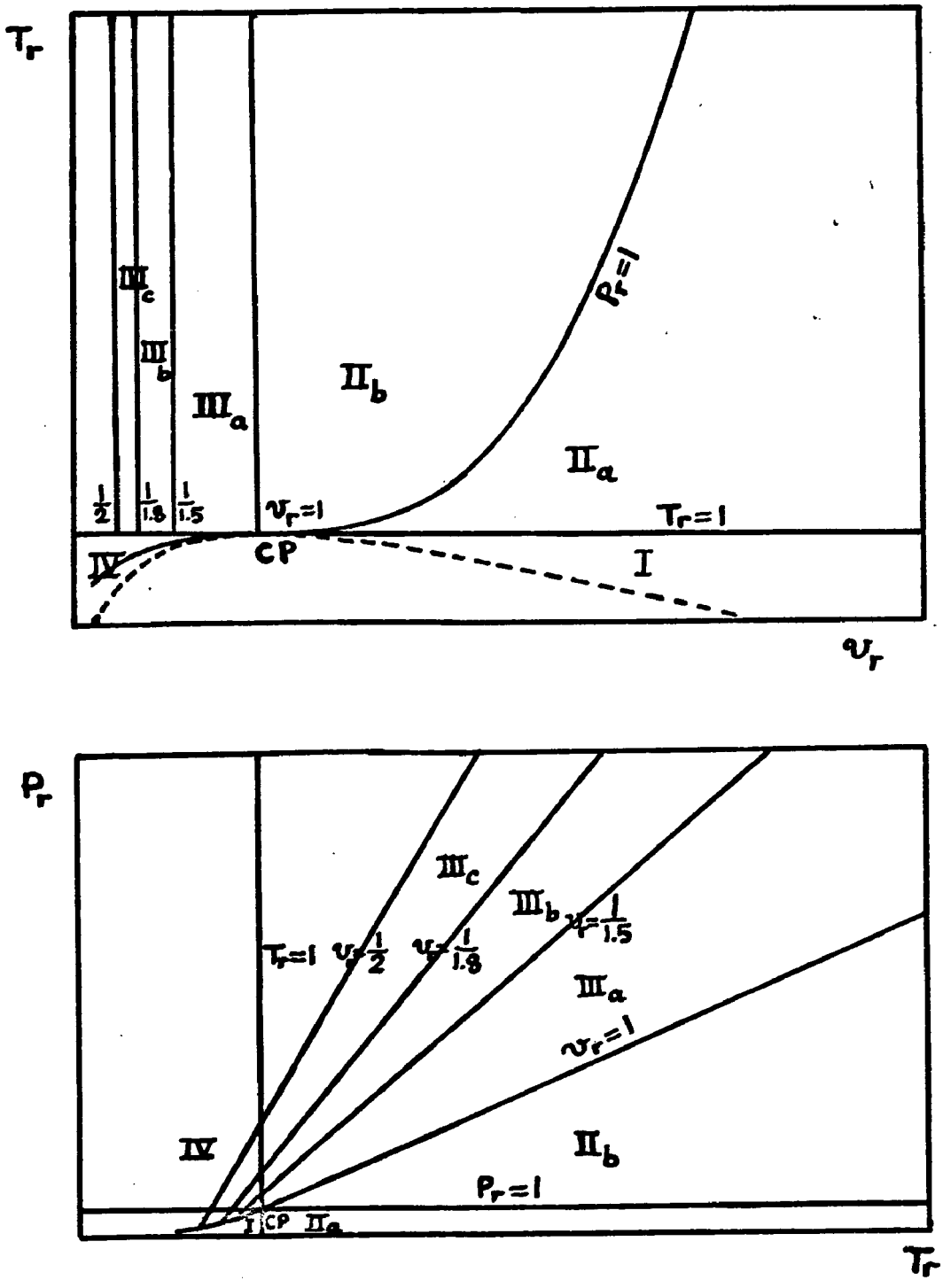


Figure 27. The regions of PvT surface for the comparison of the results

B. COMPARISONS FOR PURE SUBSTANCES

1. Comparison with the Experimental Data. The calculated pressure and the compressibility with the equation of state by using the constants determined in Chapter IV have been compared with the experimental data whose sources are listed in Table I. Table XXI illustrates the average absolute percentage deviations in different regions. It can be noted that in the low density regions (Regions I, IIa, and partly IIb), the results are reasonable, however, the agreement with the experimental data is less in the high density regions.

On the other hand, as temperature either increases from approximately 2.5 times critical temperature or decreases from the critical temperature, the fluctuation of calculated values becomes greater. Because of the method used to evaluate the constants, the critical isotherm of the equation was first fit to the available experimental data as accurately as possible. Therefore, the agreement between the equation of state and the experimental data is excellent. However, the particular character of the equation which represents isometrics is such that at high temperatures they approach straight lines rather than the slightly concaved line figuration of the experimental results. When, in this investigation, attempts were made by changing constants of the equation to improve the results of the high temperature region, it was noted that some of the greater accuracy of the temperature region closer to the critical isotherm was altered. For example, in Appendices I.1,2,3, it can be seen that in region IIb, at a temperature approximately 1.5 times critical, a negative percentage deviation was obtained in order to get better agreement at higher temperatures, or when the percentage deviation is

TABLE XXI

A COMPARISON OF THE AVERAGE ABSOLUTE DEVIATIONS BY REGIONS

Regions	ARGON			NEON			NITROGEN		
		Avg. Dev. %			Avg. Dev. %			Avg. Dev. %	
	No. of Data	This Work	(a)	No. of Data	This Work	(b)	No. of Data	This Work	(c)
I	60	0.113	0.116	30	0.210	0.463	50	0.171	0.157
IIa	112	0.066	0.057	95	0.170	0.350	157	0.063	0.054
IIb	128	0.312	0.103	130	0.418	0.517	75	0.158	0.093
IIIa	77	0.922	0.287	92	0.587	0.517	49	0.384	0.425
IIIb	33	1.513	0.592	13	0.908	1.036	20	0.881	0.346
IIIc	26	2.959	0.427	28	1.602	0.942	15	0.768	0.345
IV	28	2.062	0.393	43	17.717	3.161	25	3.319	1.421

(a) The Strobridge Equation whose constants were determined by Gosman, McCarty and Hust (35).

(b) The modified Strobridge Equation whose constants were determined by Gibbons and Kuebler (34).

(c) The Strobridge Equation whose constants were determined by Strobridge (96).

quite small at lower temperatures the deviation becomes greater at higher temperatures. If greater accuracy in the high temperature region (over 2.5 times critical temperature) is to be attained, other modifications - such as additional curvature terms - will be necessary.

The curvature term in the equation is the result of two terms: $C_r(v_r)$ which is a function only of specific volume [equation (4-25c)] and the exponential term $e^{-k(T_r-1)}$. The $C_r(v_r)$ is negative and quite small in the low density region and is positive and small between the reduced densities 1 and approximately 1.8, but is negative again at the densities higher than 1.8 times critical and rapidly becomes large as density increases. The exponential term, evidently, approaches zero as temperature increases and becomes large at low temperatures. Consequently, it may easily be pointed out that a systematic deviation originates from the form of the equation of state at high temperatures and lower than the critical temperature.

In regions I and IV, because $T_r < 1$, the exponential term becomes larger and more effective as temperature decreases. Therefore, the percentage deviation is quite negative in region I, although $C_r(v_r)$ is small. However, down to the reduced temperature of 0.8, the result is quite acceptable. In region IV, because the deviation increases rapidly, the equation of state is not satisfactory at the reduced temperatures lower than about 0.9.

In regions IIa, IIb, IIIa, IIIb, and IIIc, because $T_r > 1$ the exponential term approaches zero as the temperature increases, the slope term $B_r(v_r)$ [equation (4-25b)] is therefore more important. When the slope was decreased in order to get better results at high temperatures,

the deviation became negative at moderate and lower temperatures. To attain an optimum result was attempted in this work, but in order to do that it was necessary to decrease the slope of the isometrics at higher densities and, thereby, the curvature term became more important. Then, of course, the results were less reasonable.

2. Comparison with other Equations of State. The percentage deviation for other equations [the Strobridge equation for argon (35) and nitrogen (96), and the modified Strobridge equation for neon (34)], which may represent the PvT behavior of that particular pure substance better than the other equations, are given in Appendices I.1,2,3 for each data point. These appendices illustrate the fact that the accuracy of the equation of state near the critical isotherm is much greater than any other equation of state.

A comparison of the average absolute percentage deviation in different regions between this work and those equations is shown in Table XXI. In regions I and IIa the results are comparable. Because the high temperature for argon and neon is about 3 times critical and because the deviation is large at high temperatures, the average absolute deviation in the other regions becomes worse than the other equations. It should be noted that it is possible to obtain better results at the temperatures near the critical without testing high temperature data in region IIb, IIIa and high pressure data in regions IIIb, IIIc.

In fact, this equation of state excellently represents the PvT behavior around the critical isotherm and in the low density regions and fairly represents the behavior in the moderate to high density regions

at the temperatures up to 1.5 and 2 times critical. Therefore, the thermodynamic properties such as enthalpy, entropy, etc. may be determined by means of this equation with the given constants more accurately than the other equations around the critical isotherm and overall temperatures up to moderate densities.

C. COMPARISONS FOR MIXTURES

1. General. As mentioned previously (Chapter IV, Part C) a new combining rule which has been derived from the theory of corresponding states was used to determine the reduced constants of the equation of state for mixtures. Simultaneously, the pseudo-critical constants of mixtures were needed in order to predict the mixture properties by using the equation of state in either the reduced or non-reduced form. The linear combining rule, because of its simplicity, was used in order to correlate the pseudo-critical compressibility, specific volume, and temperature. On the other hand, the pseudo-critical temperature was also correlated by means of the linear square root combining rule because it has been utilized by several investigators. Then, the results obtained by means of both of the combining rules were compared.

The calculated values of the pseudo-critical constants were listed in Table XXII and were plotted from those values on the pressure-temperature diagram (Figure 28).

The pseudo-critical temperature correlated from the linear combining rule is larger than that from the linear square-root combining rule. Although the difference between the two calculated pseudo-critical temperatures for the argon-nitrogen system is small, it is large for the argon-neon and neon-nitrogen systems because of the critical tempera-

TABLE XXII

PSEUDO-CRITICAL CONSTANTS FOR MIXTURES TESTED IN THIS WORK

System	Argon-Nitrogen			Argon-Neon	Neon-Nitrogen
Composition	79.85% Ar 20.15% N_2	51.55% Ar 48.45% N_2	20.10% Ar 79.90% N_2	46.82% Ar 53.18% Ne	51.40% Ne 48.60% N_2
Z_{cm}(a)	0.2912	0.2913	0.2914	0.2959	0.2959
v_{cm}(b)	77.691	82.089	86.976	57.108	65.245
(c1)	145.891	138.912	131.157	94.245	84.155
T_{cm}(c2)	145.714	138.637	130.980	86.383	78.936
(d1)	44.873	40.450	36.058	40.069	31.317
P_{cm}(d2)	44.819	40.370	36.010	36.727	29.375

(a), (b), (c1) by means of the linear combining rule [equations (3-96a), (3-96b), and (3-96c) respectively].

(c2) by means of the linear square-root combining rule [equation (3-97b)].

(d1), (d2) from the equation $P_{cm}v_{cm}=Z_{cm}RT_{cm}$ by using the above values of the pseudo-critical constants (c1 and c2 respectively).

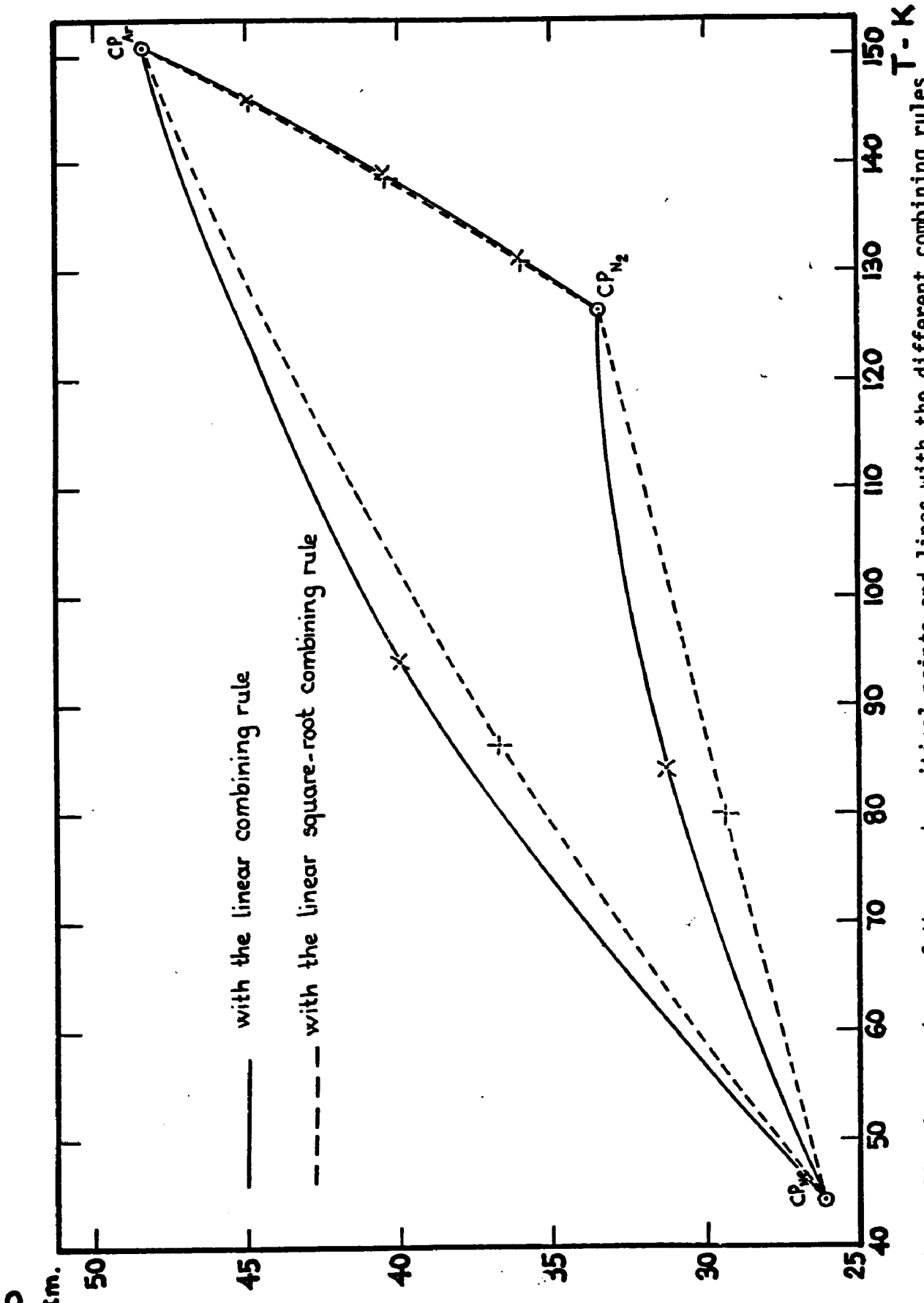


Figure 28. A comparison of the pseudo-critical points and lines with the different combining rules for temperature.

tures of the pure components. The other fact is that the maximum difference for any system is at 50%-50% composition for binary systems. Evidently, the pseudo-critical pressure changes linearly depending on the pseudo-critical temperatures, when the others are held constant. However, the calculated pressure increases, although both the pseudo-critical constants (temperature and pressure) decrease with the use of the linear square-root combining rule.

2. Comparison with Experimental Data. The equation of state for mixtures was tested with the PvT properties of the argon-nitrogen system whose data were collected by Crain, Sonntag, and Van Wylen (26) for the three different compositions, and of the argon-neon and neon-nitrogen systems whose data were obtained as a part of this work (Table XXIII).

Appendices II.1a, 1b, 1c (the argon-nitrogen system), II.2 (argon-neon system), and II.3 (neon-nitrogen system) illustrate the calculated values of the pressure, compressibility, and their percentage deviation from the experimental values at the same specific volume and temperature with the experimental data, by using the linear combining rule for the pseudo-critical temperature. For the argon-nitrogen system the deviation of the calculated values from the experimental data in the low to moderate density region (Regions I, IIa, and partly IIb) is negligibly small. In other words, the agreement with the experimental data is excellent. In the moderate density region (Regions IIb and partly III) the deviation increases with the pressure and temperature similar to that for pure substances. The deviation is larger for the composition of approximately 50% argon and 50% nitrogen than the other compositions of the argon-nitrogen system. For the argon-neon and neon nitrogen systems,

TABLE XXIII

A COMPARISON OF AVERAGE ABSOLUTE DEVIATIONS FOR MIXTURES

	I	IIa	IIb	III
ARGON-NITROGEN[a1]:				
48) 79.85% - 20.15%				
No. of Data	16	40	18	10
Avg. Dev. % - This Work (b1)	0.066	0.051	0.157	1.318
- This Work (b2)	0.065	0.044	0.216	1.396
- Other Eqn. (c)	0.934	0.095	0.494	1.500
45) 51.55% - 48.45%				
No. of Data		55	21	14
Avg. Dev. % - This Work (b1)		0.072	0.363	2.792
- This Work (b2)		0.054	0.248	2.625
- Other Eqn. (c)		0.152	0.709	2.478
42) 20.10% - 79.90%				
No. of Data		52	24	14
Avg. Dev. % - This Work (b1)		0.054	0.216	1.193
- This Work (b2)		0.046	0.147	1.070
- Other Eqn. (c)		0.101	0.437	1.172
ARGON-NEON[a2]:				
55) 46.82% - 53.18%				
No. of Data		7	6	
Avg. Dev. % - This Work (b1)		0.248	1.527	
- This Work (b2)		1.637	3.818	
- Other Eqn. (c)		1.303	3.360	
NEON-NITROGEN[a2]:				
65) 51.40% - 48.60%				
No. of Data		5	7	
Avg. Dev. % - This Work (b1)		0.720	1.000	
- This Work (b2)		2.075	4.328	
- Other Eqn. (c)		0.187	0.471	

(a1) Data from Crain, Sonntag and Van Wylen (26)
(a2) Data obtained in this research

(b1), (b2) Using linear and linear square-root combining rules respectively for the pseudo-critical temperature.

(c) BWR equation with the constants in Table VI and the combining rule listed in Table V.

the calculated values are in less satisfactory agreement with the experimental data.

The results are summarized in Table XXIII by different systems and regions. In Table XXIII a comparison of the calculated values using the linear or linear square-root combining rules for the pseudo-critical temperature is given. When the linear square-root combining rule is used the average absolute deviation for the argon-nitrogen system becomes slightly better, but for the argon-neon and neon-nitrogen systems the deviation increases.

The other combining rules for the pseudo-critical constants and the tremendous amount of combinations for the constants of the equation of state may be considered and may be tested. The results obtained in this work, at least, will be in reference to those works.

3. Comparison with Other Equations of State. For the same experimental PvT data, the percentage deviation is determined for the BWR equation of state, which is usually supposed to give better representation of the PvT behavior of mixtures than other equations, with given constants (Table VI) and with the fully tested combining rules (Table V). These deviations for each data point are also listed in Appendices II.1a, 1b,1c,2,3 for comparison. Generally, in the low to moderate density regions the modified Martin equation gives more accurate representation than the BWR equation for the argon-nitrogen and argon-neon systems. However, in the high density region for the argon-nitrogen system and in the moderate density region for the neon-nitrogen system, with available data, the results are comparable.

It should be noted that the predicted values of mixtures are dependent upon the constants of pure components and the combining rules. These results are not final, but they are the first results for this equation of state. By means of the redetermination of the pure component constants with a better agreement with the experimental data, and with the different combining rules, either for the pseudo-critical constants or for the constants of the equation of state, better agreement for mixtures may be obtained.

APPENDIX I.1

ARGON

11) Crain-Sonntag data (24)

12) Michels-Levelt-DeGraaff data (63)

13) Michels-Wijker-Wijker data (64)

14) Rogovaya-Kaganer data (79)

(*) The Strobridge Equation whose constants were determined by Gosman, McCarty, and Hust (35).

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
12335	150.650	107.6292	47.3995	47.3699	0.413	0.412	-0.062	-0.302
12135	150.150	107.6005	46.7605	46.7408	0.408	0.408	-0.042	-0.263
12225	150.650	126.9561	46.1451	46.1217	0.474	0.474	-0.051	-0.446
12024	149.650	126.8901	45.1065	45.0978	0.466	0.466	-0.019	-0.387
12924	149.150	126.8635	44.5810	44.5834	0.462	0.462	0.005	-0.348
12824	148.650	133.6257	44.0500	43.6383	0.483	0.478	-0.935	-1.305
12325	150.650	150.9104	43.9527	43.9618	0.537	0.537	0.021	-0.429
12624	148.150	150.7222	41.8870	41.9083	0.519	0.520	0.051	-0.356
12524	146.150	150.5760	40.1873	40.2441	0.505	0.505	0.141	-0.217
12614	148.150	189.2808	38.4909	38.5141	0.599	0.600	0.060	-0.306
12414	145.650	189.0618	36.9445	36.9692	0.584	0.585	0.067	-0.269
12114	143.150	188.8335	35.3570	35.4026	0.568	0.569	0.129	-0.160
11084	143.150	197.1772	34.7567	34.8156	0.583	0.584	0.170	-0.109
12604	148.150	235.3662	34.4514	34.4682	0.667	0.667	0.049	-0.213
12104	143.150	234.8571	32.1105	32.1225	0.642	0.642	0.037	-0.178
12703	139.650	234.4933	30.4267	30.4425	0.623	0.623	0.052	-0.096
12594	148.150	297.0488	29.8401	29.8452	0.729	0.729	0.017	-0.136
12094	143.150	296.4426	28.1006	28.0977	0.709	0.709	-0.010	-0.133
12393	138.150	295.8242	26.3195	26.3081	0.687	0.687	-0.043	-0.089
12093	136.150	295.5701	25.5912	25.5789	0.677	0.677	-0.048	-0.045
12892	135.150	295.4377	25.2274	25.2113	0.672	0.672	-0.064	-0.031
11074	143.150	315.4385	26.9876	26.9985	0.725	0.725	0.040	-0.061
12584	148.150	386.1306	24.7754	24.7748	0.787	0.787	-0.002	-0.067
12084	143.150	385.3933	23.5140	23.5068	0.771	0.771	-0.031	-0.075
12383	138.150	384.6367	22.2292	22.2134	0.754	0.754	-0.071	-0.060
12782	133.150	383.8760	20.9190	20.8896	0.735	0.734	-0.141	-0.022
12482	131.650	383.6570	20.5229	20.4854	0.729	0.728	-0.183	-0.019
12282	130.150	383.4253	20.1188	20.0782	0.722	0.721	-0.202	0.016
12574	148.150	480.3418	20.9089	20.9096	0.826	0.826	0.004	-0.016
12074	143.150	479.4524	19.9349	19.9309	0.814	0.813	-0.020	-0.025

Region 1

NO.	T=K	V=CC/MOLE	PEXP=ATM.	PCAL=ATM.	Z	ZCAL	DEV.%	DEV.% (*)
12373	138.150	478.5581	18.9462	18.9350	0.800	0.799	-0.059	-0.021
12772	133.150	477.6467	17.9406	17.9193	0.784	0.783	-0.119	0.004
12172	128.150	476.7327	16.9159	16.8801	0.767	0.765	-0.211	0.054
12072	127.150	476.5583	16.7087	16.6689	0.763	0.761	-0.238	0.065
12971	126.150	476.3647	16.4997	16.4570	0.759	0.757	-0.259	0.086
11064	143.150	504.3140	19.1494	19.1509	0.822	0.822	0.008	0.010
12564	148.150	660.2883	16.0502	16.0457	0.872	0.871	-0.028	-0.014
12064	143.150	659.1284	15.3714	15.3663	0.863	0.862	-0.033	-0.009
12363	138.150	657.9802	14.6877	14.6770	0.852	0.852	-0.073	-0.018
12762	133.150	656.8052	13.9951	13.9771	0.841	0.840	-0.128	-0.014
12162	128.150	654.1274	13.3204	13.2887	0.829	0.827	-0.238	-0.023
12561	123.150	652.9299	12.6090	12.5594	0.815	0.811	-0.393	-0.019
12461	121.650	652.5627	12.3882	12.3374	0.810	0.806	-0.410	0.027
12361	120.650	652.2947	12.2446	12.1888	0.807	0.803	-0.456	0.028
11054	143.150	805.9382	12.9196	12.9207	0.886	0.886	0.009	0.040
12554	148.150	995.0913	11.1628	11.1604	0.914	0.914	-0.022	0.005
12054	143.150	993.1631	10.7348	10.7313	0.908	0.907	-0.033	0.000
12353	138.150	991.7251	10.2993	10.2929	0.901	0.900	-0.062	-0.010
12752	133.150	990.0024	9.8625	9.8519	0.894	0.893	-0.107	-0.017
12152	128.150	988.0852	9.4215	9.4065	0.885	0.884	-0.159	-0.003
12551	123.150	986.3447	8.9749	8.9526	0.876	0.874	-0.248	0.009
12051	118.150	984.6406	8.5225	8.4903	0.866	0.862	-0.378	0.034
11044	143.150	1287.6296	8.4659	8.4666	0.928	0.928	0.008	0.039
12534	148.150	1584.3577	7.2536	7.2520	0.945	0.945	-0.022	0.003
12034	143.150	1581.7285	6.9925	6.9900	0.942	0.941	-0.035	-0.008
12333	138.150	1579.1743	6.7293	6.7256	0.937	0.937	-0.055	-0.015
12732	133.150	1576.5405	6.4638	6.4592	0.933	0.932	-0.071	-0.009
11034	143.150	2056.8596	5.4500	5.4519	0.954	0.955	0.035	0.058
11024	143.150	3285.2725	3.4717	3.4735	0.971	0.971	0.053	0.067
11014	143.150	5246.9180	2.1975	2.1987	0.982	0.982	0.053	0.062

464 NO.OF DATA POINTS : 60. AVG.DEV.% : 0.113 0.116

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
12825	153.150	151.0891	45.9776	45.9890	0.553	0.553	0.025	-0.453
12315	150.650	189.4919	40.0154	40.0392	0.613	0.614	0.060	-0.325
12815	153.150	189.7056	41.5205	41.5451	0.627	0.627	0.059	-0.332
12316	163.150	190.5509	47.3617	47.4050	0.674	0.675	0.091	-0.259
12305	150.650	235.6192	35.5999	35.6195	0.679	0.679	0.055	-0.213
12805	153.150	235.8739	36.7361	36.7576	0.689	0.690	0.058	-0.209
12306	163.150	236.8598	41.1713	41.2004	0.728	0.729	0.071	-0.141
12606	173.150	237.8412	45.4755	45.4976	0.761	0.762	0.049	-0.074
11146	163.150	242.0400	40.5632	40.5947	0.733	0.734	0.078	-0.122
11136	163.150	283.9365	36.2344	36.2354	0.768	0.768	0.003	-0.116
12295	150.650	297.3474	30.6975	30.7051	0.738	0.739	0.025	-0.131
12795	153.150	297.6497	31.5482	31.5562	0.747	0.747	0.025	-0.126
12296	163.150	298.8318	34.8832	34.8888	0.779	0.779	0.016	-0.082
12596	173.150	300.0071	38.1330	38.1257	0.805	0.805	-0.019	-0.037
12097	188.150	301.7527	42.8826	42.8477	0.838	0.837	-0.081	0.013
11157	203.150	300.3396	47.9331	47.8784	0.864	0.863	-0.114	0.053
12597	203.150	303.4832	47.5120	47.4493	0.865	0.864	-0.132	0.037
12285	150.650	386.5066	25.3993	25.3999	0.794	0.794	0.002	-0.064
12785	153.150	386.8757	26.0160	26.0199	0.801	0.801	0.015	-0.046
11126	163.150	386.0977	28.5927	28.5885	0.825	0.824	-0.015	-0.032
12286	163.150	388.3440	28.4600	28.4552	0.826	0.825	-0.017	-0.033
12586	173.150	389.7998	30.8480	30.8311	0.846	0.846	-0.055	-0.005
12087	188.150	391.9609	34.3522	34.3113	0.872	0.871	-0.119	0.022
12587	203.150	394.1211	37.7766	37.7130	0.893	0.892	-0.168	0.033
12088	223.150	396.9858	42.2376	42.1552	0.916	0.914	-0.195	0.033
12588	248.150	400.5684	47.6678	47.5838	0.938	0.936	-0.176	0.017
11147	203.150	403.6035	36.9839	36.9209	0.895	0.894	-0.170	0.032
11116	163.150	452.9937	25.0907	25.0779	0.849	0.849	-0.051	-0.038
11137	203.150	478.8306	31.6923	31.6487	0.910	0.909	-0.137	0.064
12275	150.650	480.7749	21.3914	21.3936	0.832	0.832	0.011	-0.009

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
12775	153.150	481.2302	21.8720	21.8734	0.838	0.838	0.006	-0.010
12276	163.150	482.9915	23.7695	23.7637	0.858	0.857	-0.024	-0.002
12576	173.150	484.7444	25.6261	25.6139	0.874	0.874	-0.048	0.028
12C77	188.150	487.3464	28.3608	28.3318	0.895	0.894	-0.102	0.049
12577	203.150	489.9487	31.0417	30.9947	0.912	0.911	-0.151	0.049
12078	223.150	493.4077	34.5410	34.4785	0.931	0.929	-0.181	0.041
12578	248.150	497.7400	38.8060	38.7423	0.949	0.947	-0.164	0.028
11149	273.150	522.0876	41.3750	41.3270	0.964	0.963	-0.116	0.006
13C60	273.150	525.0674	41.1505	41.1003	0.964	0.963	-0.122	0.000
13061	298.150	525.0674	45.4020	45.3772	0.974	0.974	-0.055	-0.023
14517	198.120	562.1414	26.4848	26.5226	0.916	0.917	0.143	0.324
14018	223.220	605.7271	28.4224	28.4614	0.940	0.941	0.137	0.343
11139	273.150	611.8945	35.4812	35.4385	0.969	0.967	-0.120	-0.001
11106	163.150	615.6287	19.2852	19.2776	0.887	0.886	-0.039	0.003
11127	203.150	643.4336	24.1428	24.1155	0.932	0.931	-0.113	0.069
12265	150.650	660.8574	16.3862	16.3824	0.876	0.876	-0.023	-0.009
12765	153.150	661.4175	16.7204	16.7174	0.880	0.880	-0.018	-0.001
12266	163.150	663.7244	18.0456	18.0387	0.895	0.894	-0.038	0.008
12566	173.150	666.0000	19.3456	19.3375	0.907	0.906	-0.042	0.044
12067	188.150	669.4197	21.2737	21.2513	0.922	0.921	-0.105	0.036
12567	203.150	672.8201	23.1652	23.1325	0.935	0.934	-0.141	0.037
12068	223.150	677.3574	25.6382	25.5989	0.948	0.947	-0.153	0.040
12568	248.150	681.7927	28.7142	28.6742	0.961	0.960	-0.139	0.031
14518	248.170	718.8633	27.2333	27.2517	0.961	0.962	0.068	0.233
11096	163.150	722.4456	16.7295	16.7248	0.903	0.903	-0.028	0.020
11117	203.150	763.2356	20.5770	20.5546	0.942	0.941	-0.109	0.057
11129	273.150	831.1965	26.3252	26.3004	0.976	0.975	-0.094	0.010
11119	273.150	974.1516	22.5387	22.5185	0.980	0.979	-0.090	0.005
11086	163.150	981.3425	12.6542	12.6521	0.928	0.927	-0.017	0.032
12255	150.650	995.6663	11.3793	11.3773	0.916	0.916	-0.018	0.010

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
12755	153.150	996.7874	11.5905	11.5876	0.919	0.919	-0.025	0.004
12256	163.150	1000.1345	12.4366	12.4320	0.929	0.929	-0.037	0.012
12556	173.150	1003.4951	13.2690	13.2646	0.937	0.937	-0.034	0.042
12057	188.150	1008.5017	14.5050	14.4956	0.947	0.947	-0.064	0.048
12557	203.150	1013.5215	15.7220	15.7084	0.956	0.955	-0.086	0.050
12058	223.150	1020.2249	17.3196	17.3013	0.965	0.964	-0.105	0.041
11107	203.150	1025.6296	15.5444	15.5313	0.956	0.956	-0.084	0.051
12558	248.150	1028.6353	19.2771	19.2576	0.974	0.973	-0.101	0.028
11076	163.150	1151.8997	10.8978	10.9003	0.938	0.938	0.023	0.069
13010	273.150	1178.6453	18.6919	18.6780	0.983	0.982	-0.074	0.008
13011	298.150	1178.6453	20.5018	20.4917	0.988	0.987	-0.049	-0.011
13012	323.150	1178.6453	22.3079	22.3053	0.992	0.991	-0.012	-0.023
13013	348.150	1178.6453	24.1139	24.1187	0.995	0.995	0.020	-0.042
13014	373.150	1178.6453	25.9176	25.9321	0.998	0.998	0.056	-0.056
13015	398.150	1178.6453	27.7200	27.7455	1.000	1.001	0.092	-0.069
13016	423.150	1178.6453	29.5226	29.5589	1.002	1.003	0.123	-0.085
11097	203.150	1216.4192	13.1974	13.1877	0.963	0.962	-0.074	0.045
11109	273.150	1323.2795	16.6793	16.6679	0.985	0.984	-0.068	0.007
11099	273.150	1550.8787	14.2632	14.2543	0.987	0.986	-0.062	0.003
11066	163.150	1564.0190	8.1632	8.1654	0.954	0.954	0.027	0.066
12235	150.650	1585.7036	7.3852	7.3822	0.947	0.947	-0.041	-0.016
12735	153.150	1586.9619	7.5149	7.5123	0.949	0.949	-0.035	-0.009
12836	163.150	1592.1624	8.0310	8.0278	0.955	0.955	-0.040	-0.001
12536	173.150	1597.3171	8.5416	8.5378	0.960	0.960	-0.044	0.011
12037	188.150	1605.1252	9.2991	9.2933	0.967	0.966	-0.062	0.016
12537	203.150	1612.9150	10.0464	10.0392	0.972	0.971	-0.071	0.022
12038	223.150	1623.3193	11.0284	11.0205	0.978	0.977	-0.072	0.027
11087	203.150	1634.6997	9.9146	9.9093	0.972	0.972	-0.054	0.038
12538	248.150	1636.4004	12.2347	12.2269	0.983	0.983	-0.064	0.024
11056	163.150	1836.3494	6.9986	7.0035	0.960	0.961	0.070	0.105

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
11077	203.150	1938.5188	8.3961	8.3936	0.976	0.976	-0.030	0.049
11089	273.150	2106.6997	10.5361	10.5309	0.990	0.990	-0.049	0.000
11079	273.150	2468.9988	9.0020	8.9989	0.992	0.991	-0.034	0.008
11046	163.150	2492.3887	5.2124	5.2150	0.970	0.971	0.051	0.077
11067	203.150	2605.2390	6.2862	6.2842	0.982	0.982	-0.032	0.027
12547	203.150	2667.9431	6.1424	6.1391	0.983	0.982	-0.054	0.004
12048	223.150	2684.6353	6.7294	6.7248	0.987	0.986	-0.068	-0.006
12548	248.150	2705.6509	7.4501	7.4458	0.990	0.989	-0.058	-0.004
11036	163.150	2927.2192	4.4553	4.4599	0.974	0.975	0.104	0.127
11057	203.150	3089.0894	5.3160	5.3148	0.985	0.985	-0.022	0.028
11069	273.150	3353.8687	6.6421	6.6398	0.994	0.994	-0.034	-0.003
11059	273.150	3930.6597	5.6726	5.6708	0.995	0.994	-0.031	-0.005
11026	163.150	3971.5791	3.3065	3.3090	0.981	0.982	0.077	0.093
11047	203.150	4151.9141	3.9702	3.9697	0.989	0.989	-0.012	0.025
11016	163.150	4665.8555	2.8218	2.8244	0.983	0.984	0.094	0.107
11037	203.150	4922.4258	3.3550	3.3543	0.991	0.990	-0.021	0.009
11049	273.150	5339.4258	4.1818	4.1807	0.996	0.996	-0.026	-0.008
11039	273.150	6257.5859	3.5703	3.5694	0.997	0.996	-0.024	-0.010
11027	203.150	6616.5938	2.5018	2.5015	0.993	0.993	-0.010	0.012
11017	203.150	7843.6133	2.1127	2.1126	0.994	0.994	-0.006	0.012
11029	273.150	8500.2148	2.6307	2.6301	0.998	0.997	-0.022	-0.012
11019	273.150	9961.9648	2.2454	2.2450	0.998	0.998	-0.016	-0.008

464 NO.OF DATA POINTS : 112. AVG.DEV.% : 0.066 0.057

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
13360	273.150	75.5932	281.4226	280.5959	0.949	0.946	-0.294	-0.006
13361	298.150	75.5932	328.2900	328.0283	1.014	1.014	-0.080	0.005
13362	323.150	75.5932	374.9697	375.4595	1.069	1.070	0.131	-0.010
13363	348.150	75.5932	421.2522	422.8901	1.115	1.119	0.389	0.014
13364	373.150	75.5932	467.2498	470.3208	1.154	1.161	0.657	0.048
13365	398.150	75.5932	513.0417	517.7517	1.187	1.198	0.918	0.080
13366	423.150	75.5932	558.5591	565.1819	1.216	1.230	1.186	0.127
12665	151.650	76.1230	49.8108	49.8326	0.305	0.305	0.044	0.039
12865	153.150	76.1850	52.5954	52.6627	0.319	0.319	0.128	0.118
12366	163.150	76.6177	71.2065	71.3475	0.408	0.408	0.198	0.249
12666	173.150	77.0577	89.6322	89.7104	0.486	0.487	0.087	0.252
12167	188.150	77.7133	116.8010	116.6584	0.588	0.587	-0.122	0.189
12667	203.150	78.3625	143.2890	142.9157	0.674	0.672	-0.260	0.130
12168	223.150	79.2058	177.5350	176.9393	0.768	0.765	-0.335	0.062
12668	248.150	80.2054	218.6970	218.0908	0.861	0.859	-0.277	0.011
11229	273.150	81.2587	257.7866	257.5115	0.935	0.934	-0.107	-0.015
12655	151.650	81.4487	49.7137	49.7056	0.325	0.325	-0.016	-0.038
12855	153.150	80.8226	52.3266	52.3580	0.337	0.337	0.060	0.021
12356	163.150	81.2885	69.5974	69.7026	0.423	0.423	0.151	0.103
12656	173.150	81.7583	86.5719	86.6753	0.498	0.499	0.119	0.149
12157	188.150	82.4604	111.5140	111.4963	0.596	0.595	-0.016	0.135
12657	203.150	83.1529	135.7810	135.6260	0.677	0.677	-0.114	0.105
14078	223.220	83.5905	168.3840	167.8594	0.768	0.766	-0.312	-0.077
12158	223.150	84.0583	167.0930	166.8421	0.767	0.766	-0.150	0.068
12658	248.150	85.1386	204.7169	204.5537	0.856	0.855	-0.080	0.021
14536	173.140	88.6730	83.0133	82.8974	0.518	0.517	-0.140	-0.294
14037	183.150	89.5282	97.4959	97.5768	0.581	0.581	0.083	-0.020
12645	151.650	91.2870	49.4517	49.4189	0.363	0.363	-0.066	-0.163
12845	153.150	91.3652	51.7554	51.7005	0.376	0.376	-0.106	-0.245
12346	163.150	91.8576	66.5908	66.6345	0.457	0.457	0.066	-0.190

Region IIb

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
12646	173.150	92.3454	81.0294	81.1489	0.527	0.527	0.148	-0.089
12147	188.150	93.0800	102.0920	102.2671	0.615	0.617	0.172	0.014
12647	203.150	93.8006	122.5480	122.7439	0.690	0.691	0.160	0.054
12148	223.150	94.7463	148.9620	149.2193	0.771	0.772	0.173	0.057
11186	163.150	94.9493	65.8449	65.8386	0.467	0.467	-0.010	-0.315
14557	198.120	94.2339	115.0980	115.3027	0.667	0.668	0.178	0.044
14068	223.220	94.9321	149.7840	149.0500	0.771	0.772	0.179	0.058
14588	248.170	94.3264	183.9090	184.2347	0.852	0.853	0.177	-0.022
12648	248.150	95.8945	180.7480	181.2090	0.851	0.853	0.255	0.016
11219	273.150	95.2328	215.5600	216.3181	0.916	0.919	0.352	-0.045
13260	273.150	95.4888	214.9287	215.7053	0.916	0.919	0.361	-0.042
13261	298.150	95.4888	248.0032	249.4069	0.968	0.973	0.566	-0.056
13262	323.150	95.4888	280.9585	283.0962	1.012	1.019	0.761	-0.099
13263	348.150	95.4888	313.6367	316.7805	1.048	1.059	1.002	-0.100
13264	373.150	95.4888	346.2156	350.4634	1.080	1.093	1.227	-0.116
13265	398.150	95.4888	378.5828	384.1455	1.106	1.123	1.469	-0.107
13266	423.150	95.4888	410.9479	417.8271	1.130	1.149	1.699	-0.100
11207	203.150	99.4427	116.8600	117.1598	0.697	0.699	0.257	0.036
14578	248.170	105.8212	164.1130	164.5921	0.853	0.855	0.292	-0.120
12835	153.150	107.7694	50.5551	50.4942	0.434	0.433	-0.120	-0.440
12336	163.150	108.3306	62.6468	62.6697	0.507	0.507	0.037	-0.422
12636	173.150	108.8826	74.2645	74.4182	0.569	0.570	0.207	-0.250
14526	173.140	109.7764	73.7216	74.0833	0.570	0.572	0.491	0.026
12137	198.150	109.6996	91.1624	91.4242	0.648	0.650	0.287	-0.103
12637	203.150	110.5050	107.5009	107.8565	0.713	0.715	0.331	-0.010
11176	163.150	111.3560	61.8566	61.9955	0.514	0.516	0.225	-0.256
12138	223.150	111.5667	128.5870	129.0705	0.783	0.786	0.376	0.027
12638	248.150	112.8677	153.9710	154.6954	0.853	0.857	0.470	0.004
14568	248.170	116.6856	149.2950	149.8938	0.855	0.859	0.401	-0.076
11197	203.150	118.0509	102.0950	102.4468	0.723	0.725	0.345	-0.019

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
14547	198.120	119.1207	96.3201	96.6214	0.706	0.708	0.313	-0.065
13230	273.150	119.1444	170.8086	171.9073	0.908	0.914	0.643	-0.029
13231	298.150	119.1444	195.2404	196.8434	0.951	0.959	0.821	-0.085
13232	323.150	119.1444	219.5271	221.7663	0.986	0.996	1.020	-0.137
13233	348.150	119.1444	243.6326	246.6838	1.016	1.029	1.252	-0.159
13234	373.150	119.1444	267.6519	271.5986	1.041	1.057	1.475	-0.185
13235	398.150	119.1444	291.5488	296.5129	1.063	1.081	1.703	-0.196
13236	423.150	119.1444	315.3977	321.4272	1.082	1.103	1.912	-0.214
12725	153.150	127.1207	48.6859	48.6584	0.492	0.492	-0.056	-0.507
12226	163.150	127.7509	58.4727	58.5188	0.558	0.558	0.079	-0.450
12526	173.150	128.3740	67.8600	68.0023	0.613	0.614	0.210	-0.288
12027	188.150	129.2875	81.4666	81.7011	0.682	0.684	0.288	-0.119
12527	203.150	130.1969	94.6273	94.9187	0.739	0.741	0.308	-0.035
14058	223.220	128.4528	113.7530	114.2596	0.798	0.801	0.445	0.097
11209	273.150	129.3579	157.5100	158.3741	0.909	0.914	0.549	-0.099
12028	223.150	131.3899	111.6059	111.9854	0.801	0.804	0.340	0.003
12528	248.150	132.8653	132.0390	132.6099	0.862	0.865	0.432	-0.007
14027	183.150	139.3573	73.1117	73.3396	0.678	0.680	0.312	-0.091
14558	248.170	142.9761	123.3019	123.8492	0.866	0.870	0.444	0.062
14048	223.220	150.8024	99.2481	99.4752	0.817	0.819	0.229	-0.002
11166	163.150	151.6430	53.8613	53.8935	0.610	0.610	0.060	-0.428
12326	163.150	151.8060	53.7984	53.8637	0.610	0.611	0.121	-0.366
11199	273.150	151.6130	134.8909	135.4967	0.912	0.917	0.449	-0.057
12626	173.150	152.5068	61.3263	61.4367	0.658	0.659	0.180	-0.241
12127	188.150	153.5455	72.2238	72.3761	0.718	0.720	0.211	-0.092
12627	203.150	154.5710	82.7806	82.9414	0.768	0.769	0.194	-0.028
12128	223.150	155.9258	96.3741	96.5961	0.821	0.823	0.230	0.030
12628	248.150	157.6019	112.7780	113.1252	0.873	0.876	0.308	0.022
11187	203.150	158.6699	81.1043	81.2367	0.772	0.773	0.163	-0.037
14537	198.120	167.1586	74.4737	74.6322	0.766	0.767	0.213	0.036

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
11156	163.150	177.8720	49.3001	49.3814	0.655	0.656	0.165	-0.231
14548	248.170	186.3046	96.7717	96.9331	0.885	0.887	0.167	0.045
11177	203.150	188.3260	70.7458	70.7948	0.799	0.800	0.069	0.010
12616	173.150	191.3775	52.9947	53.0547	0.714	0.715	0.113	-0.148
12117	188.150	192.6036	61.1907	61.2368	0.763	0.764	0.075	-0.052
12617	203.150	193.8187	69.1414	69.1587	0.804	0.804	0.025	-0.013
12118	223.150	195.4270	79.4122	79.4217	0.848	0.848	0.012	0.008
12618	248.150	197.4216	91.8157	91.8771	0.890	0.891	0.067	-0.004
11189	273.150	205.9629	100.6659	100.8118	0.925	0.926	0.145	-0.039
14038	223.220	210.1374	74.4409	74.5782	0.854	0.856	0.185	0.232
14516	173.140	211.0919	49.4822	49.5722	0.735	0.737	0.182	-0.013
14017	183.150	237.3989	49.8792	49.9130	0.788	0.788	0.068	0.032
12107	188.150	239.2909	51.7493	51.7432	0.802	0.802	-0.012	-0.006
12607	203.150	240.7229	57.8457	57.8101	0.835	0.835	-0.062	0.030
12108	223.150	242.6346	65.7468	65.6876	0.871	0.870	-0.090	0.037
11179	273.150	241.3930	86.5831	86.6114	0.932	0.933	0.033	-0.030
12608	248.150	245.0079	75.3158	75.2717	0.906	0.906	-0.058	0.016
14538	248.170	251.8797	73.4043	73.3775	0.908	0.908	-0.036	0.052
11167	203.150	253.1009	55.4729	55.4194	0.842	0.841	-0.096	0.017
14527	198.120	276.1826	49.6273	49.6639	0.843	0.844	0.074	0.197
13150	273.150	288.8176	73.0015	72.9734	0.941	0.940	-0.038	-0.009
13151	298.150	288.8176	81.2650	81.3150	0.959	0.960	0.062	-0.056
13152	323.150	288.8176	89.4774	89.6532	0.975	0.976	0.197	-0.083
13153	348.150	288.8176	97.6736	97.9300	0.987	0.991	0.324	-0.123
13154	373.150	288.8176	105.8408	106.3261	0.998	1.003	0.459	-0.153
13155	398.150	288.8176	113.9820	114.6622	1.008	1.014	0.597	-0.175
13156	423.150	288.8176	122.1349	122.9981	1.016	1.023	0.707	-0.217
12098	223.150	305.7859	53.5304	53.4414	0.894	0.892	-0.166	0.036
12598	248.150	308.6584	60.8380	60.7477	0.922	0.921	-0.148	0.011
14028	223.220	315.2715	52.0023	52.0117	0.895	0.895	0.018	0.227

NO.	T=K	V=CC/MOLE	PEXP=ATM.	PCAL=ATM.	Z	ZCAL	DEV.%	DEV.% (*)
11169	273.150	327.9297	64.6814	64.6286	0.946	0.946	-0.082	-0.011
14528	248.170	380.6028	49.9574	49.9343	0.934	0.933	-0.046	0.144
11159	273.150	384.3257	55.5697	55.5108	0.953	0.952	-0.106	-0.003
13062	323.150	525.0674	49.6385	49.6530	0.983	0.983	0.029	-0.039
13063	348.150	525.0674	53.8747	53.9284	0.990	0.991	0.100	-0.073
13064	373.150	525.0674	58.0956	58.2036	0.996	0.998	0.186	-0.090
13065	398.150	525.0674	62.3144	62.4788	1.001	1.004	0.264	-0.113
13066	423.150	525.0674	66.5289	66.7539	1.006	1.009	0.338	-0.134

464 NO.OF DATA POINTS : 128. AVG.DEV.% : 0.312 0.103

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
10C05	150.860	74.5600	48.3400	48.3399	0.291	0.291	-0.000	0.000
11217	203.150	74.0008	151.3909	150.8024	0.672	0.669	-0.389	0.141
14026	163.110	70.8887	72.6866	73.7404	0.385	0.391	1.450	1.605
11196	163.150	69.6880	75.1131	74.4374	0.391	0.387	-0.899	-0.732
14047	183.150	70.2378	116.6060	116.4496	0.545	0.544	-0.134	0.323
12177	188.150	69.2694	129.0829	128.7031	0.579	0.577	-0.294	0.227
14567	198.120	71.2715	146.9580	146.1060	0.644	0.641	-0.580	-0.014
12677	203.150	69.8926	160.5509	159.7764	0.673	0.670	-0.482	0.129
12178	223.150	70.6914	201.2070	200.0452	0.777	0.772	-0.577	0.050
14088	223.220	71.8896	197.6700	196.3780	0.776	0.771	-0.654	-0.044
12678	248.150	71.6195	250.0130	248.7268	0.879	0.875	-0.514	0.016
12675	151.650	67.7415	50.0255	50.1000	0.272	0.273	0.149	0.169
12875	153.150	67.7989	53.1844	53.3940	0.287	0.288	0.394	0.428
12176	158.150	68.0036	64.0251	64.3484	0.335	0.337	0.505	0.607
12376	163.150	68.2129	74.9367	75.2525	0.382	0.383	0.421	0.607
12676	173.150	68.6335	96.7569	96.8683	0.467	0.468	0.115	0.461
14546	173.140	67.3328	98.2822	98.2590	0.466	0.466	-0.024	0.331
12707	203.150	64.2651	176.6209	175.7809	0.681	0.678	-0.476	0.079
12208	223.150	65.0157	223.0120	221.8098	0.792	0.788	-0.539	0.025
12708	248.150	65.8722	278.7485	277.4490	0.902	0.898	-0.466	0.004
12705	151.650	62.1983	50.3895	50.5449	0.252	0.253	0.308	0.397
12505	153.150	62.2583	54.0069	54.2883	0.268	0.269	0.521	0.606
12406	163.150	62.6554	78.7472	79.1867	0.369	0.371	0.558	0.739
12706	173.150	63.0572	103.6789	103.8725	0.460	0.461	0.187	0.506
14556	173.140	63.6627	102.6030	102.9494	0.460	0.461	0.338	0.670
12207	188.150	63.6695	140.6289	140.2606	0.580	0.578	-0.262	0.214
14577	198.120	62.7194	169.3120	168.2903	0.653	0.649	-0.603	-0.124
11227	203.150	62.3513	183.3930	182.6386	0.686	0.683	-0.411	0.055
13450	273.150	61.0502	378.0107	378.4819	1.030	1.031	0.125	-0.001
13451	298.150	61.0502	444.6516	446.7468	1.110	1.115	0.471	0.063

Region IIIa

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
13452	323.150	61.0502	510.9333	515.0308	1.176	1.186	0.802	0.099
13453	348.150	61.0502	576.4968	583.3223	1.232	1.247	1.184	0.185
13454	373.150	61.0502	641.6550	651.6155	1.279	1.299	1.552	0.265
13455	398.150	61.0502	706.3005	719.9114	1.320	1.345	1.927	0.360
13456	423.150	61.0502	770.5481	788.2068	1.355	1.386	2.292	0.457
11206	163.150	59.4465	82.6015	82.4516	0.367	0.366	-0.181	-0.074
12188	223.150	59.4751	252.3550	251.9131	0.820	0.818	-0.175	-0.026
12688	248.150	60.2498	316.9885	316.7942	0.938	0.937	-0.061	-0.028
11239	273.150	59.8397	390.0566	391.1436	1.041	1.044	0.279	-0.009
12186	158.150	57.0300	70.2766	70.8621	0.309	0.311	0.833	0.872
12386	163.150	57.2294	84.8373	85.4207	0.363	0.365	0.688	0.701
12686	173.150	57.6232	113.8880	114.3078	0.462	0.464	0.369	0.422
12187	188.150	58.2116	156.8459	156.8266	0.591	0.591	-0.012	0.124
12687	203.150	58.7758	198.5930	198.2685	0.700	0.699	-0.163	0.010
12738	248.150	58.2862	333.8535	334.4976	0.956	0.957	0.193	-0.050
12935	153.150	55.0818	57.0745	57.4140	0.250	0.252	0.595	0.769
12436	163.150	55.4504	87.8176	88.4159	0.364	0.366	0.681	0.587
14566	173.140	55.8078	118.7219	119.1228	0.466	0.468	0.338	0.230
12736	173.150	55.8273	118.6509	119.0975	0.466	0.468	0.376	0.270
14057	183.150	56.2063	148.9920	149.3114	0.557	0.558	0.214	0.137
12237	188.150	56.3854	164.1190	164.2614	0.599	0.600	0.087	0.022
14587	198.120	56.6421	194.3309	194.1983	0.677	0.677	-0.068	-0.135
12737	203.150	56.9187	208.3420	208.2914	0.711	0.711	-0.024	-0.079
12238	223.150	57.5712	265.3147	265.3586	0.834	0.834	0.017	-0.087
12518	248.150	55.1608	365.9426	368.7375	0.991	0.999	0.764	-0.070
12216	163.150	52.2999	95.0521	95.7335	0.371	0.374	0.717	0.350
12516	173.150	52.6947	129.3300	130.0452	0.480	0.482	0.553	0.075
14067	183.150	52.9219	166.4960	166.8391	0.582	0.583	0.206	-0.390
12017	188.150	53.2698	179.5540	180.3152	0.620	0.622	0.424	-0.093
12517	203.150	53.8121	228.1910	229.1305	0.737	0.740	0.412	-0.144

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
12018	223.150	54.4620	290.7385	292.2847	0.865	0.869	0.532	-0.121
12715	153.150	51.9113	60.5604	60.8683	0.250	0.251	0.509	0.658
14036	163.110	51.3038	97.1628	98.6518	0.372	0.378	1.533	1.056
12198	223.150	51.4966	322.0857	325.8120	0.906	0.916	1.157	-0.165
12698	248.150	52.0933	405.9446	412.1101	1.038	1.054	1.519	-0.074
11249	273.150	51.0734	515.2056	527.4360	1.174	1.202	2.374	0.019
14576	173.140	50.1089	141.4650	142.7218	0.499	0.503	0.888	0.026
12197	188.150	50.4451	198.4840	200.1263	0.649	0.654	0.827	-0.198
12697	203.150	50.9286	252.4620	254.8336	0.771	0.779	0.939	-0.200
13480	273.150	50.3968	528.9011	542.6995	1.189	1.220	2.609	0.036
13481	298.150	50.3968	623.5996	643.7917	1.285	1.326	3.238	0.167
13482	323.150	50.3968	717.6028	744.9138	1.364	1.416	3.806	0.254
13483	348.150	50.3968	810.1963	846.0481	1.429	1.492	4.425	0.412
13484	373.150	50.3968	902.0171	947.1858	1.485	1.559	5.008	0.559
13485	398.150	50.3968	992.9260	1048.3264	1.532	1.617	5.580	0.720
13486	423.150	50.3968	1083.0176	1149.4670	1.572	1.668	6.136	0.889
12696	173.150	49.9158	142.6819	143.8930	0.501	0.506	0.849	-0.044

464 NO.OF DATA POINTS : 77. AVG.DEV.% : 0.922 0.287

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
12895	153.150	49.1912	66.0128	66.2742	0.258	0.259	0.396	0.429
12396	163.150	49.5541	104.5860	105.4343	0.387	0.390	0.811	0.128
14077	183.150	49.0501	190.5410	191.3823	0.622	0.625	0.442	-0.762
12218	223.150	48.3761	366.1467	373.1545	0.967	0.986	1.914	-0.201
12718	248.150	48.8337	462.0876	473.4197	1.108	1.135	2.452	-0.084
14015	153.150	46.6252	73.7184	75.1931	0.273	0.279	2.000	1.812
14046	163.110	47.5427	113.4299	115.5312	0.403	0.410	1.852	0.904
12716	173.150	47.1094	162.5549	164.2355	0.539	0.545	1.034	-0.296
12217	188.150	47.5421	225.6470	228.4801	0.695	0.704	1.256	-0.323
12717	203.150	47.9310	286.8716	291.2356	0.825	0.837	1.521	-0.278
12915	153.150	46.4898	75.6252	75.8141	0.280	0.280	0.250	0.051
12416	163.150	46.8029	119.4340	120.4341	0.418	0.421	0.837	-0.197
14586	173.140	46.6576	167.9660	168.2969	0.552	0.553	0.197	-1.185
11237	203.150	46.4779	308.1016	313.8652	0.859	0.875	1.871	-0.229
14056	163.110	45.9152	125.2600	126.7543	0.430	0.435	1.193	0.052
14025	153.150	44.2351	91.4429	89.3509	0.322	0.314	-2.288	-2.727
14596	173.140	44.4288	192.2890	193.2375	0.601	0.604	0.493	-1.143
12227	188.150	44.3948	269.3516	273.7373	0.774	0.787	1.628	-0.414
12727	203.150	44.8104	338.2996	345.2212	0.909	0.928	2.046	-0.333
12228	223.150	45.2720	427.3667	438.5649	1.057	1.084	2.620	-0.218
12728	248.150	45.7394	534.9856	552.8357	1.202	1.242	3.337	-0.079
12925	153.150	43.1880	98.1528	98.2883	0.337	0.338	0.138	-0.422
14066	163.110	43.2687	151.9489	153.4621	0.491	0.496	0.996	-0.354
12426	163.150	43.5577	148.8390	150.1089	0.484	0.488	0.853	-0.485
11216	163.150	43.7052	152.3780	148.3545	0.497	0.484	-2.640	-3.925
12726	173.150	43.9120	197.9810	200.4238	0.612	0.619	1.234	-0.450
12247	188.150	42.2438	312.6936	318.1875	0.856	0.871	1.757	-0.364
12747	203.150	42.6175	389.1067	397.9788	0.995	1.017	2.280	-0.279
12248	223.150	43.0258	488.0117	502.6262	1.147	1.181	2.995	-0.162
12748	248.150	43.4370	607.6826	631.1763	1.296	1.346	3.866	-0.029

Region IIIb

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
14035	153.150	41.7678	113.2840	114.2021	0.376	0.380	0.810	0.133
14076	163.110	41.6476	176.2890	177.4883	0.549	0.552	0.680	-0.656
12746	173.150	41.7961	233.8610	236.7748	0.688	0.696	1.246	-0.436

464 NO.OF DATA POINTS : 33. AVG.DEV.% : 1.513 0.592

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
12945	153.150	41.0902	123.4090	123.7353	0.403	0.405	0.264	-0.438
14045	153.150	41.1593	123.1180	122.6966	0.403	0.402	-0.342	-1.038
12446	163.150	41.4574	179.5290	181.0681	0.556	0.561	0.857	-0.472
12757	203.150	40.2940	463.6946	473.7019	1.121	1.145	2.158	-0.180
12258	223.150	40.6436	575.4875	592.7119	1.277	1.316	2.993	-0.090
12758	248.150	40.9956	710.8005	739.4685	1.431	1.489	4.033	0.026
14055	153.150	39.9449	143.3889	143.4715	0.456	0.456	0.058	-0.640
12456	163.150	39.2674	228.1180	229.6151	0.669	0.673	0.656	-0.342
12756	173.150	39.5765	288.9177	291.8259	0.805	0.813	1.007	-0.302
12257	188.150	39.9720	377.5396	383.3662	0.977	0.993	1.543	-0.259
11247	203.150	39.2167	507.4617	518.1208	1.194	1.219	2.100	0.074
13625	398.150	39.8344	1674.3616	1838.9868	2.041	2.242	9.832	1.301
13626	423.150	39.8344	1816.8987	2011.6787	2.084	2.308	10.720	1.582
14065	153.150	38.8545	166.5100	167.5302	0.515	0.518	0.613	-0.009
12955	153.150	38.9199	165.5679	165.9173	0.513	0.514	0.211	-0.415
12767	203.150	38.0824	564.9478	573.0295	1.291	1.309	1.431	-0.067
12268	223.150	38.3740	692.0857	708.3103	1.450	1.484	2.344	-0.005
12768	248.150	38.6710	845.7595	875.6560	1.606	1.663	3.535	0.104
12466	163.150	37.2064	298.3586	298.8320	0.829	0.830	0.159	-0.105
12766	173.150	37.4779	366.7117	367.9934	0.967	0.971	0.350	-0.102
12267	188.150	37.8098	467.0706	470.9961	1.144	1.153	0.840	-0.074
13560	273.150	37.5693	1105.9182	1151.0220	1.854	1.929	4.078	0.314
13561	298.150	37.5693	1280.6846	1347.2026	1.967	2.069	5.194	0.512
13562	323.150	37.5693	1453.5242	1543.3611	2.059	2.187	6.181	0.640
13563	348.150	37.5693	1622.2214	1739.5115	2.133	2.288	7.230	0.885
13564	373.150	37.5693	1788.9043	1935.6553	2.195	2.375	8.203	1.114

464 NO.OF DATA POINTS : 26. AVG.DEV.% : 2.959 0.427

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
12405	150.650	62.1584	48.0580	48.0491	0.242	0.242	-0.018	0.078
12385	150.650	56.7532	48.8780	48.9307	0.224	0.225	0.108	0.398
12435	150.650	54.9950	49.5730	49.6386	0.221	0.221	0.132	0.500
12215	150.650	51.8141	52.0415	52.0923	0.218	0.218	0.098	0.571
12914	149.150	51.7591	47.0144	46.8155	0.199	0.198	-0.423	0.327
12514	148.150	51.7259	43.6952	43.2932	0.186	0.184	-0.920	0.061
12395	150.650	49.1006	56.3956	56.3924	0.224	0.224	-0.006	0.451
12694	148.150	49.0143	46.8665	46.4731	0.189	0.187	-0.839	0.279
12415	150.650	46.4128	64.6079	64.5306	0.243	0.242	-0.120	0.150
12714	148.150	46.3372	53.6249	53.1989	0.204	0.203	-0.794	0.197
12514	145.650	46.2613	42.7408	41.8287	0.165	0.162	-2.134	0.038
12314	144.650	46.2316	38.4332	37.2695	0.150	0.145	-3.028	-0.168
12425	150.650	43.0912	85.2439	85.0946	0.297	0.297	-0.175	-0.341
12724	148.150	42.9983	72.2701	71.7493	0.256	0.254	-0.721	-0.302
12224	143.150	42.8209	46.0712	44.6556	0.168	0.163	-3.073	-0.200
12923	140.750	42.7262	33.5359	31.5490	0.124	0.117	-5.925	-0.265
12445	150.650	40.9973	109.0850	109.0504	0.362	0.362	-0.032	-0.450
12744	148.150	40.9047	94.6078	94.2049	0.318	0.317	-0.426	-0.445
12244	143.150	40.7096	65.2632	64.1501	0.226	0.222	-1.706	-0.215
12543	138.150	40.5251	35.4376	33.2669	0.127	0.119	-6.125	0.112
12243	137.150	40.4622	29.4772	27.2705	0.106	0.098	-7.486	0.955
12455	150.650	38.8270	149.5519	149.6862	0.470	0.470	0.090	-0.404
12754	148.150	38.7323	133.3790	133.2941	0.425	0.425	-0.064	-0.386
12254	143.150	38.5438	100.4612	99.8445	0.330	0.328	-0.614	-0.365
14013	138.120	38.0933	72.8372	70.6808	0.245	0.238	-2.960	-1.713
12553	138.150	38.3510	66.7774	65.5531	0.226	0.222	-1.833	-0.186
12952	133.150	38.1590	32.3317	30.2101	0.113	0.106	-6.562	0.428
12652	131.650	38.1014	21.8604	19.3876	0.077	0.068	-11.312	1.022

464 NO.OF DATA POINTS : 28. AVG.DEV.% : 2.062 0.393

ALL DATA HAVE BEEN PROCESSED

STOP 0
EXECUTION TERMINATED

Region IV

APPENDIX I.2

NEON

21) Scott-Sonntag data (82)

22)
23) Gibbons data (33)

24) Sullivan-Sonntag data (100)

(*) The modified Strobridge equation whose constants were determined by Gibbons and Kuebler (34).

Region I

NO.	T=K	V=CC/MOLE	PEXP=ATM.	PCAL=ATM.	Z	ZCAL	DEV.%	DEV.% (*)
23115	44.229	66.8604	25.0405	25.0248	0.461	0.461	-0.062	0.271
23015	44.359	82.6460	23.8962	23.8970	0.543	0.543	0.003	-0.328
23014	43.241	82.6890	22.1688	22.2364	0.517	0.518	0.305	0.069
21949	44.002	85.7901	23.0847	23.0818	0.548	0.548	-0.012	-0.400
21948	43.100	85.7246	21.7801	21.8071	0.528	0.529	0.124	-0.191
22914	42.562	104.7752	19.6492	19.6589	0.589	0.590	0.050	-0.568
21344	44.007	107.9189	20.9081	20.9588	0.625	0.626	0.243	-0.445
21343	43.000	107.9132	19.8412	19.8859	0.607	0.608	0.226	-0.439
21351	41.989	107.8959	18.7138	18.7963	0.586	0.589	0.441	-0.172
21253	44.014	163.3325	16.4070	16.3848	0.742	0.741	-0.135	-0.873
21252	41.999	163.2796	15.1039	15.0886	0.716	0.715	-0.101	-0.784
21251	40.008	163.2401	13.7661	13.7743	0.684	0.685	0.059	-0.456
22715	44.142	233.5980	12.6298	12.6395	0.814	0.815	0.077	-0.555
22724	42.124	233.5275	11.7876	11.7915	0.796	0.797	0.033	-0.545
22714	40.092	233.5320	10.8393	10.9172	0.769	0.775	0.719	0.279
21355	44.002	236.5842	12.4393	12.4559	0.815	0.816	0.133	-0.493
21354	42.004	236.5288	11.6229	11.6271	0.798	0.798	0.036	-0.533
21353	40.000	236.4733	10.7774	10.7787	0.776	0.777	0.012	-0.412
22723	39.080	237.4919	10.3931	10.3497	0.770	0.766	-0.417	-0.729
22713	37.674	237.4625	9.8530	9.7367	0.757	0.748	-1.180	-1.252
22524	42.996	364.8884	8.4237	8.4366	0.871	0.873	0.153	-0.303
22514	41.052	364.7639	7.9352	7.9417	0.859	0.860	0.082	-0.302
22523	39.131	364.6357	7.4521	7.4448	0.846	0.845	-0.097	-0.342
22513	37.112	364.5046	6.9148	6.9118	0.828	0.827	-0.043	-0.028
22315	44.162	579.9260	5.7732	5.7674	0.924	0.923	-0.101	-0.438
22324	42.078	579.8271	5.4583	5.4494	0.917	0.915	-0.163	-0.466
22314	40.116	579.6296	5.1634	5.1479	0.909	0.906	-0.300	-0.534
22323	38.193	579.4233	4.8660	4.8488	0.900	0.896	-0.353	-0.466
22312	34.097	579.0085	4.1859	4.1951	0.866	0.868	0.219	0.676
22313	36.019	579.2751	4.4855	4.5046	0.879	0.883	0.427	0.547

431 NO.OF DATA POINTS : 30. AVG.DEV.% : 0.210 0.463

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
21329	44.394	42.4225	26.0616	26.1696	0.303	0.305	0.414	1.738
21337	44.401	52.2443	25.8626	26.0898	0.371	0.374	0.879	2.097
21240	44.395	63.0581	25.3870	25.6009	0.439	0.443	0.842	1.366
23016	45.401	82.4185	25.4481	25.4536	0.563	0.563	0.022	-0.359
21950	45.013	86.0536	24.5122	24.4723	0.571	0.570	-0.163	-0.603
21951	46.001	85.7793	25.8988	25.8795	0.589	0.588	-0.074	-0.535
22916	45.808	104.3144	23.2310	23.2790	0.645	0.646	0.207	-0.454
21345	44.406	107.9247	21.3304	21.3802	0.632	0.633	0.234	-0.457
21346	45.001	107.9420	21.9583	22.0044	0.642	0.643	0.210	-0.480
21347	46.005	107.9478	23.0128	23.0520	0.658	0.659	0.171	-0.508
21348	48.002	107.9651	25.0460	25.1088	0.686	0.688	0.251	-0.380
22817	50.752	155.1576	21.3680	21.4152	0.796	0.798	0.221	-0.377
22827	52.183	155.2055	22.2667	22.3338	0.807	0.809	0.302	-0.248
22837	53.556	155.2395	23.1425	23.2113	0.817	0.820	0.297	-0.206
22847	54.855	155.2727	23.9766	24.0373	0.827	0.829	0.253	-0.210
22818	56.555	155.3181	25.0391	25.1129	0.838	0.840	0.295	-0.121
22828	58.126	155.3640	26.0218	26.1020	0.848	0.850	0.308	-0.070
21254	45.995	163.3589	17.6570	17.6354	0.764	0.763	-0.122	-0.849
21255	50.012	163.4382	20.1533	20.1129	0.803	0.801	-0.201	-0.819
21256	59.997	163.5973	26.1809	26.0918	0.870	0.867	-0.340	-0.677
22716	46.112	233.6796	13.4389	13.4533	0.830	0.831	0.107	-0.526
22726	48.080	233.7587	14.2327	14.2558	0.843	0.845	0.163	-0.443
22717	50.122	233.8306	15.0802	15.0803	0.857	0.857	0.001	-0.559
21356	45.992	236.6397	13.2569	13.2680	0.831	0.832	0.084	-0.546
21357	49.999	236.7507	14.8869	14.8738	0.859	0.858	-0.088	-0.647
21358	59.998	236.9731	18.8328	18.7879	0.906	0.904	-0.239	-0.560
24146	70.000	241.9780	22.3139	22.2234	0.940	0.936	-0.406	-0.610
24156	70.000	288.8647	18.8712	18.8008	0.949	0.945	-0.373	-0.564
24147	80.000	272.3677	23.2603	23.1892	0.965	0.962	-0.306	-0.488
24157	80.000	325.1877	19.5856	19.5304	0.970	0.967	-0.282	-0.441

Region IIa

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
24148	100.000	335.9575	24.2283	24.1919	0.992	0.990	-0.150	-0.381
22617	50.528	358.1245	10.4844	10.4917	0.906	0.906	0.069	-0.371
22627	52.064	358.2231	10.8562	10.8742	0.910	0.912	0.166	-0.249
22637	53.528	358.3083	11.2004	11.2376	0.914	0.917	0.332	-0.056
22647	54.598	358.3308	11.4002	11.5037	0.912	0.920	0.908	0.537
22618	57.055	358.5134	12.0867	12.1088	0.926	0.927	0.182	-0.142
22628	58.083	358.5488	12.3413	12.3625	0.928	0.930	0.172	-0.136
22638	59.641	358.6340	12.7237	12.7453	0.932	0.934	0.170	-0.113
22619	61.595	358.7375	13.2069	13.2246	0.937	0.939	0.134	-0.121
22629	62.739	358.7805	13.4888	13.5054	0.940	0.941	0.123	-0.117
22639	64.158	358.8398	13.8438	13.8532	0.944	0.944	0.068	-0.157
22649	65.681	358.9045	14.2217	14.2259	0.947	0.947	0.030	-0.179
22659	67.208	359.0374	14.5790	14.5966	0.949	0.950	0.121	-0.074
22669	68.680	359.1135	14.9498	14.9556	0.953	0.953	0.039	-0.145
22679	70.224	359.2021	15.3253	15.3314	0.955	0.956	0.040	-0.134
24166	70.000	344.8386	15.9367	15.8842	0.957	0.954	-0.329	-0.507
22516	45.091	364.9583	8.9506	8.9641	0.883	0.884	0.151	-0.332
22526	47.105	365.0698	9.4419	9.4648	0.892	0.894	0.243	-0.236
22536	49.137	365.1643	9.9463	9.9662	0.901	0.903	0.200	-0.257
22517	51.453	365.3167	10.5143	10.5324	0.910	0.911	0.172	-0.249
24176	70.000	411.6567	13.4429	13.4040	0.963	0.961	-0.290	-0.454
24167	80.000	388.2537	16.4790	16.4380	0.975	0.972	-0.248	-0.391
24158	100.000	401.1646	20.3086	20.2816	0.993	0.992	-0.133	-0.324
24149	120.000	401.5227	24.6269	24.6181	1.004	1.004	-0.036	-0.325
24186	70.000	491.4216	11.3265	11.2989	0.969	0.967	-0.243	-0.395
24177	80.000	463.5505	13.9561	13.8266	0.978	0.976	-0.213	-0.341
24168	100.000	479.0286	17.0217	17.0030	0.994	0.993	-0.110	-0.271
24159	120.000	479.4766	20.6036	20.5967	1.003	1.003	-0.033	-0.272
22419	70.047	557.6035	10.0029	10.0040	0.970	0.970	0.011	-0.132
24187	80.000	553.4478	11.6434	11.6233	0.982	0.980	-0.173	-0.289

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
22316	46.144	580.1235	6.0757	6.0664	0.931	0.929	-0.153	-0.497
22326	48.091	580.2546	6.3625	6.3590	0.936	0.935	-0.056	-0.393
22317	50.040	580.4265	6.6612	6.6499	0.942	0.940	-0.169	-0.491
24196	70.000	586.6406	9.5353	9.5156	0.974	0.972	-0.207	-0.345
24178	100.000	572.0056	14.2673	14.2535	0.995	0.994	-0.097	-0.235
24169	120.000	572.5647	17.2411	17.2365	1.002	1.002	-0.027	-0.226
22117	50.634	669.8757	5.8944	5.8865	0.950	0.949	-0.135	-0.419
22127	52.412	670.0764	6.1165	6.1134	0.953	0.952	-0.050	-0.318
22137	53.569	670.1750	6.2623	6.2610	0.955	0.955	-0.020	-0.276
22147	54.821	670.2886	6.4247	6.4205	0.957	0.957	-0.066	-0.309
22118	56.581	670.4790	6.6530	6.6439	0.961	0.959	-0.136	-0.362
22128	59.297	670.7344	6.9875	6.9884	0.963	0.963	0.012	-0.188
22119	61.012	670.9006	7.2126	7.2054	0.967	0.966	-0.100	-0.285
22129	62.156	671.0063	7.3473	7.3501	0.967	0.967	0.038	-0.138
22139	63.514	671.1260	7.5179	7.5217	0.968	0.969	0.051	-0.115
22149	65.121	671.2795	7.7310	7.7246	0.971	0.970	-0.083	-0.238
22159	66.509	671.3955	7.8854	7.8998	0.970	0.972	0.183	0.036
22179	70.093	671.6489	8.3524	8.3524	0.975	0.975	-0.000	-0.129
24206	70.000	700.3137	8.0208	8.0072	0.978	0.976	-0.170	-0.295
24197	80.000	660.7805	9.7805	9.7659	0.984	0.983	-0.149	-0.254
24188	100.000	683.0283	11.9583	11.9475	0.995	0.994	-0.090	-0.211
24179	120.000	683.7246	14.4303	14.4271	1.002	1.002	-0.022	-0.191
21359	60.314	883.6685	5.4409	5.4495	0.971	0.973	0.159	-0.001
21959	70.072	817.1250	6.8915	6.8932	0.979	0.980	0.024	-0.091
24216	70.000	836.0095	6.7438	6.7332	0.981	0.980	-0.157	-0.270
24207	80.000	788.9285	8.2123	8.2016	0.987	0.986	-0.130	-0.226
24198	100.000	815.6025	10.0211	10.0135	0.996	0.995	-0.075	-0.181
24189	120.000	816.4707	12.0791	12.0770	1.002	1.001	-0.017	-0.161
24217	80.000	941.9307	6.8930	6.8851	0.989	0.988	-0.115	-0.202
24208	100.000	973.9075	8.3973	8.3918	0.997	0.996	-0.065	-0.159

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
24199	120.000	974.9854	10.1135	10.1107	1.001	1.001	-0.028	-0.152
21360	60.234	1553.7329	3.1284	3.1317	0.983	0.984	0.106	-0.003
21960	70.060	1459.3630	3.8925	3.8938	0.988	0.988	0.032	-0.050
21259	69.998	3800.9412	1.5051	1.5044	0.996	0.995	-0.047	-0.097
21260	69.225	6683.1055	0.8471	0.8477	0.997	0.997	0.076	0.035

431 NO.OF DATA POINTS : 95. AVG.DEV.% : 0.170 0.350

Region IIb

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
21330	45.000	42.4252	28.0262	28.2158	0.322	0.324	0.677	1.525
21331	46.000	42.4316	31.3698	31.5907	0.353	0.355	0.704	0.991
23216	46.694	43.1138	33.7339	33.7694	0.380	0.380	0.105	0.163
23206	45.697	43.1240	30.4834	30.4746	0.351	0.350	-0.029	0.444
23226	47.708	43.1423	37.0001	37.1080	0.408	0.409	0.292	0.074
23236	48.717	43.1490	40.3302	40.4328	0.435	0.436	0.254	-0.139
23217	50.205	43.1705	45.3193	45.3246	0.475	0.475	0.012	-0.524
21101	49.993	47.3123	42.6066	42.5220	0.491	0.490	-0.199	-0.592
21102	69.991	47.3756	100.3202	100.3323	0.828	0.828	0.012	-0.944
21937	44.998	47.9065	27.9058	27.8926	0.362	0.362	-0.062	0.927
21938	45.997	47.9167	30.8521	30.7736	0.392	0.391	-0.254	0.239
21939	47.991	47.9577	36.5627	36.4981	0.445	0.444	-0.177	-0.266
21940	50.006	47.9406	42.2858	42.2788	0.494	0.494	-0.017	-0.397
21941	55.005	48.0170	56.4699	56.4925	0.601	0.601	0.040	-0.576
21942	60.005	47.9976	70.5892	70.7206	0.688	0.689	0.186	-0.514
21944	64.994	48.0342	84.6024	84.8167	0.762	0.764	0.253	-0.567
21943	69.992	48.0857	98.5165	98.8652	0.825	0.828	0.354	-0.650
24056	70.000	49.1530	97.2274	96.7768	0.832	0.828	-0.463	-1.519
24047	80.000	46.2840	133.0937	132.5236	0.938	0.934	-0.428	-1.761
24038	100.000	47.7520	184.1213	185.1411	1.071	1.077	0.554	-2.168
24029	120.000	47.7770	239.0719	242.0211	1.160	1.174	1.234	-2.781
21338	45.005	52.2523	27.6142	27.6577	0.391	0.391	0.158	1.044
21339	46.000	52.2627	30.3089	30.2326	0.420	0.419	-0.252	0.224
23246	45.091	55.2041	27.7940	27.6744	0.415	0.413	-0.430	0.290
23256	45.919	55.1829	29.7904	29.6797	0.436	0.435	-0.372	0.062
23266	46.827	55.2095	31.9414	31.8652	0.459	0.458	-0.238	-0.046
23276	47.850	55.1882	34.3297	34.3277	0.483	0.482	-0.006	-0.015
23286	48.821	55.2166	36.6840	36.6466	0.506	0.505	-0.102	-0.255
23296	49.684	55.2030	38.7965	38.7124	0.525	0.524	-0.217	-0.468
23247	51.199	55.2249	42.3772	42.3133	0.557	0.556	-0.151	-0.531

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
23257	52.004	55.2374	44.0450	44.2201	0.570	0.572	0.398	-0.037
24066	70.000	58.6740	81.6516	81.7865	0.834	0.835	0.165	-1.098
24057	80.000	55.2569	109.3310	109.9026	0.920	0.925	0.523	-1.351
24048	100.000	57.0150	148.9023	151.2222	1.035	1.051	1.558	-1.725
24039	120.000	57.0450	191.4889	195.8896	1.109	1.135	2.298	-2.288
23127	51.295	60.0189	40.6628	40.6761	0.580	0.580	0.033	-0.332
23137	53.183	60.0493	44.3260	44.6819	0.610	0.615	0.803	0.338
23147	54.596	60.0752	47.5327	47.6643	0.637	0.639	0.277	-0.245
23118	56.118	60.0944	50.6216	50.8700	0.661	0.664	0.491	-0.093
23128	59.185	60.1259	56.8842	57.3064	0.704	0.709	0.742	0.034
23119	60.907	60.1547	60.4135	60.8980	0.727	0.733	0.802	0.019
23129	62.142	60.1691	62.9062	63.4734	0.742	0.749	0.902	0.061
23139	63.848	60.1948	66.4137	67.0191	0.763	0.770	0.912	-0.012
23149	65.169	60.2077	69.1391	69.7666	0.778	0.785	0.908	-0.084
23159	66.697	60.2264	72.2334	72.9363	0.795	0.803	0.973	-0.101
23169	68.209	60.2473	75.2268	76.0656	0.810	0.819	1.115	-0.046
23179	70.081	60.2711	79.0128	79.9362	0.828	0.838	1.169	-0.103
21241	44.994	63.0659	26.9028	26.8344	0.460	0.458	-0.254	0.102
21242	46.006	63.0798	29.0375	28.9075	0.485	0.483	-0.448	-0.306
21243	48.003	63.0896	33.0616	32.9662	0.530	0.528	-0.288	-0.418
21244	50.002	63.1034	37.0491	36.9913	0.570	0.569	-0.156	-0.445
21245	54.993	63.1469	46.9047	46.9198	0.656	0.657	0.032	-0.480
21246	59.997	63.1904	56.6121	56.7611	0.727	0.729	0.263	-0.443
21247	65.003	63.2319	66.2615	66.5388	0.785	0.789	0.419	-0.524
21248	70.000	63.2835	75.8069	76.2428	0.835	0.840	0.575	-0.648
23116	46.001	66.9098	28.4663	28.4043	0.505	0.503	-0.218	-0.209
23126	47.736	66.9562	31.6855	31.6721	0.542	0.541	-0.042	-0.217
23136	49.514	66.9994	35.0153	34.9869	0.577	0.577	-0.081	-0.371
23117	51.381	67.0277	38.4033	38.4416	0.611	0.611	0.100	-0.271
24076	70.000	70.0420	69.2561	69.4410	0.844	0.847	0.267	-0.821

NO.	T=K	V=CC/MOLE	PEXP=ATM.	PCAL=ATM.	Z	ZCAL	DEV.%	DEV.% (*)
24067	80.000	65.9699	91.0234	91.7888	0.915	0.922	0.841	-0.970
24058	100.000	68.0770	122.0946	124.1983	1.013	1.030	1.723	-1.351
24049	120.000	68.1140	155.5557	159.3524	1.076	1.102	2.441	-1.838
23026	46.303	82.4459	26.7331	26.7672	0.580	0.581	0.128	-0.283
23036	47.369	82.4615	28.2546	28.3096	0.599	0.601	0.195	-0.235
23046	48.354	82.4888	29.6588	29.7219	0.617	0.618	0.213	-0.224
23056	49.623	82.5150	31.4837	31.5296	0.638	0.639	0.146	-0.291
23017	50.410	82.5179	32.5968	32.6471	0.650	0.651	0.154	-0.280
23027	51.731	82.5327	34.3974	34.5110	0.669	0.671	0.330	-0.101
24086	70.000	83.6120	58.9992	59.0613	0.859	0.860	0.105	-0.691
24077	80.000	78.7620	76.4044	76.9083	0.917	0.923	0.660	-0.767
24068	100.000	81.2869	100.9979	102.3935	1.000	1.014	1.382	-1.086
24059	120.000	81.3330	127.5737	130.1486	1.054	1.075	2.018	-1.479
21952	47.995	85.8522	28.6319	28.6122	0.624	0.624	-0.069	-0.541
21953	50.003	85.8230	31.3503	31.3451	0.656	0.656	-0.016	-0.475
21954	55.001	85.9217	37.9761	37.9974	0.723	0.723	0.056	-0.368
21955	59.991	85.9546	44.4791	44.5528	0.777	0.778	0.166	-0.295
21946	65.002	85.9656	50.9500	51.0894	0.821	0.823	0.274	-0.303
21956	70.004	86.0279	57.3344	57.5535	0.859	0.862	0.382	-0.371
22927	52.800	98.8436	31.7643	31.8853	0.725	0.727	0.381	-0.085
22918	55.007	98.8929	34.2018	34.3242	0.749	0.752	0.358	-0.067
22928	56.771	98.9187	36.0920	36.2636	0.766	0.770	0.475	0.070
22938	58.943	98.9660	38.4237	38.6339	0.786	0.790	0.547	0.152
22919	60.486	98.9914	40.1152	40.3129	0.800	0.804	0.493	0.096
22929	62.074	99.0199	41.7894	42.0348	0.812	0.817	0.587	0.179
22939	63.739	99.0584	43.5808	43.8319	0.825	0.830	0.576	0.148
22949	65.133	99.0911	45.1246	45.3326	0.837	0.840	0.461	0.012
22959	66.567	99.1076	46.6021	46.8802	0.846	0.851	0.597	0.119
22969	67.918	99.1291	48.0497	48.3337	0.855	0.860	0.591	0.083
22979	69.039	99.1490	49.2396	49.5372	0.862	0.867	0.605	0.068

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
24096	70.000	99.8130	50.3235	50.2699	0.874	0.874	-0.107	-0.658
24087	80.000	94.0350	64.3973	64.6129	0.922	0.926	0.335	-0.679
24078	100.000	97.0610	84.0062	84.7759	0.994	1.003	0.916	-0.908
24069	120.000	97.1190	105.2952	106.8254	1.038	1.054	1.453	-1.204
22926	48.935	104.4048	26.5201	26.6211	0.690	0.692	0.381	-0.208
22917	52.201	104.4645	29.9238	30.0431	0.730	0.733	0.399	-0.095
21349	49.991	108.0056	27.1046	27.1247	0.714	0.714	0.074	-0.494
21350	54.994	108.0576	32.0950	32.1130	0.769	0.769	0.056	-0.375
24106	70.000	119.1519	42.9013	42.7865	0.890	0.888	-0.267	-0.659
24097	80.000	112.2700	54.3665	54.3991	0.930	0.930	0.060	-0.634
24088	100.000	115.8969	70.1102	70.4704	0.990	0.995	0.514	-0.786
24079	120.000	115.9700	87.2889	88.1203	1.028	1.038	0.952	-0.998
24116	70.000	142.2400	36.5347	36.3919	0.905	0.901	-0.391	-0.691
24107	80.000	134.0419	45.9233	45.8606	0.938	0.936	-0.137	-0.616
24098	100.000	138.3900	58.6309	58.7639	0.989	0.991	0.227	-0.693
24089	120.000	138.4820	72.5757	72.9962	1.021	1.027	0.579	-0.839
22838	59.646	155.4034	26.9824	27.0562	0.857	0.859	0.274	-0.073
22819	61.660	155.4632	28.2345	28.3151	0.868	0.870	0.285	-0.028
22829	62.683	155.4921	28.8886	28.9530	0.873	0.875	0.223	-0.078
22839	64.456	155.5390	29.9967	30.0570	0.882	0.884	0.201	-0.083
22849	65.697	155.5689	30.7802	30.8288	0.888	0.890	0.158	-0.118
22859	67.150	155.6036	31.6506	31.7311	0.894	0.896	0.254	-0.017
22869	68.713	155.6443	32.6443	32.6995	0.901	0.903	0.169	-0.101
22879	70.018	155.6786	33.4633	33.5071	0.907	0.908	0.131	-0.141
21257	70.013	163.7432	32.1047	31.9804	0.915	0.911	-0.387	-0.645
24126	70.000	169.8000	31.0483	30.9183	0.918	0.914	-0.419	-0.669
24117	80.000	160.0359	38.7807	38.6845	0.945	0.943	-0.248	-0.594
24108	100.000	165.2490	49.0917	49.1115	0.989	0.989	0.040	-0.618
24099	120.000	165.3640	60.4697	60.6627	1.015	1.019	0.319	-0.717
21958	70.005	195.0237	27.2883	27.1946	0.926	0.923	-0.343	-0.571

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
24136	70.000	202.7020	26.3430	26.2317	0.930	0.926	-0.422	-0.645
24127	80.000	191.0720	32.7298	32.6314	0.953	0.950	-0.301	-0.565
24118	100.000	197.3220	41.1338	41.1042	0.989	0.988	-0.072	-0.556
24109	120.000	197.4660	50.4512	50.5301	1.012	1.013	0.156	-0.613
24137	80.000	228.1260	27.6038	27.5158	0.959	0.956	-0.319	-0.533
24128	100.000	235.6180	34.4771	34.4330	0.990	0.989	-0.128	-0.494
24119	120.000	235.8000	42.1355	42.1587	1.009	1.010	0.055	-0.528
24138	100.000	281.3506	28.9013	28.8583	0.991	0.989	-0.149	-0.435
24129	120.000	281.5786	35.2140	35.2135	1.007	1.007	-0.001	-0.453
24139	120.000	336.2446	29.4441	29.4352	1.005	1.005	-0.030	-0.388

431 NO. OF DATA POINTS : 130. AVG. DEV.% : 0.418 0.517

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
20005	44.400	41.7440	26.1900	26.1899	0.300	0.300	-0.000	1.271
24046	70.000	41.1770	118.1366	116.2829	0.847	0.834	-1.569	-1.992
21322	44.401	40.0790	26.2056	26.1943	0.288	0.288	-0.043	1.091
21323	44.997	40.0822	28.2802	28.3692	0.307	0.308	0.315	0.974
24028	100.000	39.9960	232.6842	230.5378	1.134	1.124	-0.922	-2.558
24019	120.000	40.0170	304.7886	303.8777	1.239	1.235	-0.299	-3.168
23316	45.338	39.1574	29.7002	29.7272	0.313	0.313	0.091	0.440
23326	46.751	39.2078	34.8540	35.0521	0.356	0.358	0.568	0.316
23336	47.845	39.2274	38.9009	39.1697	0.389	0.391	0.691	0.195
21230	44.995	38.6455	28.4782	28.4846	0.298	0.298	0.023	0.529
21231	46.001	38.6536	32.2896	32.3543	0.331	0.331	0.201	0.161
21232	48.003	38.6736	39.9872	40.0554	0.393	0.393	0.171	-0.386
21233	49.998	38.6885	47.7962	47.7324	0.451	0.450	-0.133	-0.828
21234	55.002	38.7226	67.3852	66.9864	0.578	0.575	-0.592	-1.132
21235	60.006	38.7524	87.0443	86.2264	0.685	0.679	-0.940	-1.256
21236	64.995	38.7605	106.3962	105.4456	0.773	0.766	-0.893	-1.097
21237	70.004	38.8023	125.9350	124.6068	0.851	0.842	-1.055	-1.264
24037	80.000	38.7710	166.1444	163.2850	0.981	0.964	-1.721	-2.183
23317	52.183	38.2014	56.3088	56.7410	0.502	0.506	0.768	0.086
23327	53.715	38.2242	62.4808	62.7363	0.542	0.544	0.409	-0.199
23337	54.734	38.2349	66.5362	66.7272	0.566	0.568	0.287	-0.266
23318	56.497	38.2552	73.4210	73.6235	0.606	0.608	0.276	-0.183
23328	58.115	38.2726	79.7963	79.9481	0.640	0.642	0.190	-0.188
23319	61.530	38.3109	93.2115	93.2702	0.707	0.708	0.063	-0.185
23329	62.745	38.3226	98.0771	98.0072	0.730	0.729	-0.071	-0.287
23339	64.101	38.3372	103.4812	103.2847	0.754	0.753	-0.190	-0.379
23349	66.226	38.3579	111.9345	111.5514	0.790	0.787	-0.342	-0.509
23359	67.108	38.3687	115.4248	114.9710	0.804	0.801	-0.393	-0.557
23369	68.615	38.3861	121.2065	120.8113	0.826	0.824	-0.326	-0.493
23379	70.044	38.3999	126.8917	126.3530	0.848	0.844	-0.425	-0.603

Region IIIa

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
21315	44.404	35.8115	26.4843	26.2768	0.260	0.258	-0.783	-0.183
21316	45.008	35.8109	28.9261	28.8897	0.280	0.280	-0.126	0.023
21317	45.997	35.8096	32.9718	33.1745	0.313	0.315	0.615	0.277
21933	44.415	34.8783	26.4362	26.3825	0.253	0.252	-0.203	0.263
21932	45.023	34.8988	29.0537	29.1267	0.274	0.275	0.251	0.278
21931	46.022	34.9048	33.4016	33.6421	0.309	0.311	0.720	0.282
21930	48.012	34.9108	42.2785	42.6553	0.375	0.378	0.891	0.081
21929	50.006	34.9338	51.3707	51.6815	0.437	0.440	0.605	-0.231
21928	54.981	34.9719	74.2784	74.2294	0.576	0.575	-0.066	-0.582
21927	59.984	34.9925	97.4216	96.9436	0.693	0.689	-0.491	-0.697
21926	64.971	35.0071	120.5221	119.6001	0.791	0.785	-0.765	-0.810
21925	69.983	35.0369	143.6276	142.2682	0.876	0.868	-0.946	-0.963
24036	70.000	34.4970	149.0674	145.5548	0.895	0.874	-2.356	-2.376
23416	45.179	33.7943	30.0009	30.1431	0.273	0.275	0.474	0.286
23426	46.186	33.8174	34.5599	34.9480	0.308	0.312	1.123	0.534
23436	47.258	33.8124	39.5236	40.0842	0.345	0.349	1.418	0.613
23446	48.171	33.8220	43.8394	44.4522	0.375	0.380	1.398	0.516
23456	49.171	33.8316	48.6965	49.2385	0.408	0.413	1.113	0.217
23417	50.129	33.8459	53.4593	53.8167	0.440	0.443	0.669	-0.198
23427	50.954	33.8502	57.3377	57.7716	0.464	0.468	0.757	-0.069
23437	52.131	33.8647	62.9148	63.3984	0.498	0.502	0.769	0.021
24018	100.000	33.5020	304.2402	299.9768	1.242	1.225	-1.401	-2.692
23447	52.824	32.7139	68.8842	69.5516	0.520	0.525	0.969	0.240
23457	54.383	32.7353	76.9120	77.4746	0.564	0.568	0.732	0.122
23418	55.974	32.7532	85.0280	85.5622	0.606	0.610	0.628	0.134
23428	57.419	32.7673	92.3843	92.9076	0.642	0.646	0.566	0.166
23438	59.039	32.7816	100.7319	101.1405	0.682	0.684	0.406	0.096
23419	60.349	32.7928	107.5656	107.7937	0.712	0.714	0.212	-0.037
23429	61.703	32.8060	114.4416	114.6555	0.741	0.743	0.187	-0.010
23439	63.068	32.8221	121.5190	121.5497	0.771	0.771	0.025	-0.131

NO.	T=K	V=CC/MOLE	PEXP=ATM.	PCAL=ATM.	Z	ZCAL	DEV.%	DEV.% (*)
23449	64.491	32.8362	128.8734	128.7412	0.800	0.799	-0.103	-0.227
23459	66.060	32.8539	136.8078	136.6460	0.829	0.828	-0.118	-0.221
23469	67.993	32.8744	146.6956	146.3743	0.864	0.862	-0.219	-0.312
23479	70.027	32.8957	157.1479	156.5909	0.900	0.896	-0.354	-0.455
23425	44.424	32.4513	26.8137	26.7850	0.239	0.238	-0.107	0.067
23466	45.167	32.4651	30.4228	30.6027	0.266	0.268	0.591	0.289
23476	46.085	32.4733	34.9018	35.3253	0.300	0.303	1.214	0.557
24027	80.000	32.4790	216.3159	211.9013	1.070	1.048	-2.041	-2.431
21305	44.407	30.8514	27.3432	27.2653	0.231	0.231	-0.285	-0.204
21306	44.994	30.8557	30.5518	30.5999	0.255	0.256	0.158	-0.145
21307	46.004	30.8679	36.2087	36.3359	0.296	0.297	0.352	-0.350
21308	48.002	30.8755	47.4659	47.7128	0.372	0.374	0.520	-0.460
21309	50.005	30.8935	59.0528	59.1085	0.445	0.445	0.094	-0.874
21310	54.994	30.9261	88.2367	87.5190	0.605	0.600	-0.813	-1.484
23518	56.610	29.6099	103.0068	104.1915	0.657	0.664	1.150	0.380
23528	59.783	29.6435	122.6567	123.8106	0.741	0.748	0.941	0.273
23519	61.679	29.6607	134.4175	135.5222	0.788	0.794	0.822	0.190
23529	63.010	29.6758	142.6971	143.7019	0.819	0.825	0.704	0.088
23539	64.518	29.6917	152.1149	152.9625	0.853	0.858	0.557	-0.051
23549	65.852	29.6996	160.4473	161.2023	0.882	0.886	0.471	-0.141
23559	67.644	29.7137	171.6432	172.2201	0.919	0.922	0.336	-0.290
23569	69.337	29.7374	181.8212	182.4891	0.950	0.954	0.367	-0.281
24026	70.000	28.9040	201.1379	197.3662	1.012	0.993	-1.875	-2.767
21218	44.405	28.3036	29.5409	29.5666	0.229	0.230	0.087	0.149
21219	44.995	28.3068	33.4164	33.6027	0.256	0.258	0.558	0.227
21220	46.004	28.3127	40.1146	40.5060	0.301	0.304	0.976	0.230
21221	47.997	28.3254	53.5398	54.1391	0.385	0.389	1.119	0.040
21222	50.003	28.3389	67.2605	67.8531	0.465	0.469	0.881	-0.261
21223	54.997	28.3740	101.8043	101.9265	0.640	0.641	0.120	-0.909
21224	59.999	28.3872	135.8200	136.1446	0.783	0.785	0.239	-0.708

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
21225	64.993	28.4056	169.9257	170.2064	0.905	0.907	0.165	-0.799
21226	70.000	28.4360	204.1185	204.0989	1.010	1.010	-0.010	-1.076

431 NO.OF DATA POINTS : 92. AVG.DEV.% : 0.587 0.596

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
24017	80.000	27.2120	301.6135	300.0876	1.250	1.244	-0.506	-2.498
21917	45.024	24.8327	47.4052	47.0878	0.319	0.316	-0.669	-1.336
21918	46.014	24.8495	56.2613	56.2181	0.370	0.370	-0.077	-1.094
21919	48.017	24.8584	74.6909	74.8417	0.471	0.472	0.202	-1.193
21920	50.007	24.8715	92.7406	93.2656	0.562	0.565	0.566	-1.011
21921	55.008	24.8899	138.3505	139.5964	0.763	0.770	0.901	-0.892
21922	59.987	24.9111	183.2097	185.5072	0.927	0.939	1.254	-0.713
21923	64.981	24.9358	227.9538	231.2858	1.066	1.082	1.462	-0.713
23615	44.663	24.0495	49.4042	49.8197	0.324	0.327	0.841	0.083
23616	46.125	24.0648	63.6022	64.4507	0.404	0.410	1.334	0.128
23626	47.897	24.0836	80.7216	82.1198	0.495	0.503	1.732	0.239
23617	50.602	24.1185	107.2787	108.8686	0.623	0.632	1.482	-0.225
24016	70.000	24.2220	302.5439	300.1853	1.276	1.266	-0.780	-3.347

431 NO.OF DATA POINTS : 13. AVG.DEV.% : 0.908 1.036

Region IIIb

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
23627	53.610	23.0102	159.5172	162.3678	0.834	0.849	1.787	-0.050
23637	54.952	23.0203	175.2610	177.2214	0.895	0.905	1.119	-0.766
23618	56.536	23.0476	190.4734	194.2852	0.946	0.965	2.001	0.025
23628	57.650	23.0585	202.2924	206.4673	0.986	1.006	2.064	0.033
23746	49.354	22.9643	113.9323	115.3249	0.646	0.654	1.222	-0.412
23718	50.428	22.9766	124.6326	127.2246	0.692	0.706	2.080	0.378
23728	52.020	22.9971	142.5602	144.7549	0.768	0.780	1.539	-0.224
23767	50.042	22.2809	137.1469	138.8103	0.744	0.753	1.213	-0.332
23777	51.037	22.2916	148.5058	150.6344	0.790	0.802	1.433	-0.140
23787	52.025	22.3026	159.7176	162.3390	0.834	0.848	1.641	0.034
23797	53.060	22.3128	171.5997	174.6094	0.879	0.895	1.754	0.111
23738	53.995	22.3214	182.4459	185.6902	0.919	0.935	1.778	0.100
23748	54.665	22.3270	190.4733	193.6366	0.948	0.964	1.661	-0.042
23758	55.567	22.3389	200.4141	204.1782	0.982	1.000	1.878	0.132
21211	46.000	22.1626	96.2299	92.0780	0.565	0.541	-4.314	-5.729
21212	48.008	22.1704	121.0117	116.6408	0.681	0.656	-3.612	-5.034
21213	49.996	22.1806	145.4310	140.8572	0.786	0.762	-3.145	-4.595
21214	55.010	22.2079	206.0996	201.6550	1.014	0.992	-2.156	-3.761
23746	49.990	21.4772	160.5836	161.7145	0.841	0.847	0.704	-0.507
23737	51.006	21.4887	173.2871	174.7979	0.890	0.897	0.872	-0.326
23747	52.011	21.4997	185.4365	187.7234	0.934	0.946	1.233	0.031
23757	53.094	21.5025	199.2368	201.9604	0.983	0.997	1.367	0.158
23715	44.596	21.0533	100.9175	102.0848	0.581	0.587	1.157	-0.631
23716	46.169	21.0710	122.1369	123.3224	0.679	0.686	0.971	-0.421
23726	47.839	21.0924	146.0914	145.7061	0.785	0.783	-0.264	-1.398
23736	49.033	21.1058	160.8193	161.7243	0.844	0.848	0.563	-0.474
23717	50.949	21.1267	186.4127	187.3657	0.942	0.947	0.511	-0.430
23727	52.190	21.1414	202.1975	203.8716	0.998	1.006	0.828	-0.094

431 NO. OF DATA POINTS : 28. AVG. DEV.% : 1.602 0.942

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
23315	44.259	39.1360	25.7945	25.6614	0.278	0.277	-0.516	0.650
21229	44.395	38.6403	26.2901	26.1774	0.279	0.278	-0.429	0.553
23415	44.091	33.7830	25.2287	24.9484	0.236	0.233	-1.111	-0.494
21217	43.988	28.3000	26.7839	26.7161	0.210	0.209	-0.253	0.190
23515	44.397	27.1780	31.5892	31.6604	0.236	0.236	0.226	0.277
23524	43.923	27.1726	28.1956	28.1063	0.213	0.212	-0.317	0.177
23514	43.545	27.1675	24.7944	25.2722	0.189	0.192	1.927	2.914
21916	44.018	24.8394	38.2699	37.6367	0.263	0.259	-1.655	-1.724
21915	42.008	24.8192	20.5361	18.9330	0.148	0.136	-7.806	-4.655
23624	43.136	24.0289	34.5903	34.5233	0.235	0.234	-0.194	0.045
23614	42.139	24.0151	25.1165	24.5037	0.174	0.170	-2.440	-0.785
23734	40.959	22.5797	24.8041	24.4285	0.167	0.164	-1.514	-1.584
23724	40.652	22.5751	21.3979	20.8626	0.145	0.141	-2.502	-2.207
23714	40.413	22.5703	17.6842	18.0972	0.120	0.123	2.336	3.051
21210	43.990	22.1497	71.4441	67.5493	0.438	0.414	-5.451	-6.881
21209	42.002	22.1324	46.8569	43.3024	0.301	0.278	-7.586	-9.051
21208	39.998	22.1164	22.0576	18.7580	0.149	0.126	-14.959	-16.397
23733	39.790	21.6840	22.2130	22.7838	0.148	0.151	2.570	-1.840
23723	39.509	21.6803	18.5812	19.2079	0.124	0.128	3.373	-1.786
23713	39.209	21.6755	14.8951	15.4003	0.100	0.104	3.391	-2.893
23734	43.006	21.0300	79.0936	80.7083	0.471	0.481	2.042	-0.451
23724	41.454	21.0088	57.8696	59.7205	0.357	0.369	3.198	-0.586
23714	40.056	20.9890	38.5884	40.7726	0.246	0.260	5.660	-0.641
23713	38.669	20.9669	19.1603	21.9771	0.127	0.145	14.701	0.525
21913	50.002	20.2909	214.3497	210.8099	1.060	1.042	-1.651	-1.848
21912	46.012	20.2708	153.5848	151.6575	0.825	0.814	-1.255	-2.342
21911	44.001	20.2588	123.1632	121.8715	0.691	0.684	-1.049	-3.075
21910	42.011	20.2492	92.4501	92.2743	0.543	0.542	-0.190	-3.910
21909	40.002	20.2366	61.2816	62.4873	0.378	0.385	1.967	-5.418
21908	38.073	20.2277	31.0220	33.7697	0.201	0.219	8.857	-9.448

Region IV

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
23816	45.478	19.2690	198.3022	197.3685	1.024	1.019	-0.471	-1.046
23815	44.396	19.2561	180.0514	180.1503	0.952	0.952	0.055	-1.277
23874	43.269	19.2425	159.8970	162.1867	0.867	0.879	1.432	-0.931
23864	41.831	19.2237	135.0198	139.2950	0.756	0.780	3.166	-1.018
23854	40.454	19.2062	111.0936	117.2784	0.643	0.679	5.567	-1.233
23844	39.387	19.1892	91.9312	100.3692	0.546	0.596	9.179	-0.744
23834	38.309	19.1735	72.6190	83.1531	0.443	0.507	14.506	-0.323
23893	37.553	19.1613	59.3180	71.1169	0.369	0.442	19.891	-0.298
23883	36.275	19.1417	36.9645	50.6532	0.238	0.326	37.032	-1.071
23873	35.465	19.1288	22.7049	37.6694	0.149	0.248	65.909	-2.245
23863	35.147	19.1233	17.0878	32.5852	0.113	0.216	90.693	-3.139
23882	34.794	19.1158	10.8648	27.0059	0.073	0.181	148.563	-4.912
23872	34.442	19.1105	5.8540	21.3225	0.040	0.144	264.238	-31.274

431 NO.OF DATA POINTS : 43. AVG.DEV.% : 17.717 3.161

ALL DATA HAVE BEEN PROCESSED

STOP 0
EXECUTION TERMINATED

APPENDIX I.3

NITROGEN

31) Sonntag-Öztürk data (88)

32) Friedman data (31)

33) Crain-Sonntag data (24)

34) Canfield-Leland-Kobayashi data (18)

35) Weber data (103)

36) Streett-Stavely data (95)

(*) The Strobridge equation whose constants were determined by Strobridge (96).

Region 1

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
32045	126.190	107.8529	33.4600	33.4338	0.348	0.348	-0.078	0.212
32055	126.190	127.2439	33.1700	33.1156	0.408	0.407	-0.164	0.277
32065	126.190	130.5040	33.0800	33.0276	0.417	0.416	-0.158	0.268
32575	126.030	129.9631	32.9100	32.8717	0.414	0.413	-0.116	0.322
32415	125.750	129.4836	32.7700	32.5831	0.411	0.409	-0.570	-0.115
32615	126.110	133.7532	32.8800	32.8477	0.425	0.425	-0.098	0.313
32075	126.190	148.9839	32.3900	32.3563	0.466	0.466	-0.104	0.174
32565	126.030	148.3640	32.2500	32.2376	0.463	0.462	-0.038	0.256
32414	125.230	145.8839	31.6700	31.5945	0.450	0.449	-0.238	0.133
32085	126.190	159.0340	31.8700	31.8889	0.489	0.490	0.059	0.252
32555	126.030	158.5043	31.7600	31.7811	0.487	0.487	0.066	0.274
32095	126.190	169.3249	31.3400	31.3567	0.512	0.513	0.053	0.170
32545	126.030	169.0847	31.2900	31.2463	0.512	0.511	-0.140	-0.012
32105	126.190	190.1549	30.1600	30.1752	0.554	0.554	0.050	0.057
32535	126.030	189.8852	30.1200	30.0847	0.553	0.552	-0.117	-0.101
32425	125.750	189.0852	30.0000	29.9438	0.550	0.549	-0.187	-0.152
32424	125.230	187.0949	29.7200	29.7029	0.541	0.541	-0.058	0.017
32115	126.190	207.7760	29.1100	29.1257	0.584	0.584	0.054	0.005
32525	126.030	207.1258	29.0300	29.0695	0.581	0.582	0.136	0.097
32125	126.190	238.7170	27.2800	27.2908	0.629	0.629	0.040	-0.051
32515	126.030	238.0365	27.2100	27.2507	0.626	0.627	0.150	0.065
32435	125.750	237.4065	27.1500	27.1472	0.625	0.625	-0.010	-0.083
32413	120.030	235.4469	24.3200	24.3187	0.581	0.581	-0.005	0.273
32434	125.230	306.2285	23.3300	23.3325	0.695	0.695	0.011	-0.049
32135	126.190	317.4187	23.1300	23.1490	0.709	0.710	0.082	-0.000
32423	120.030	366.6797	19.2500	19.2136	0.717	0.715	-0.189	-0.047
32145	126.190	417.7207	19.1600	19.1591	0.773	0.773	-0.005	-0.043
32412	110.030	468.0525	14.0600	13.9750	0.729	0.725	-0.604	0.129
32433	120.030	680.1187	12.1600	12.1557	0.840	0.839	-0.036	0.073
32155	126.190	754.4207	11.9300	11.9286	0.869	0.869	-0.012	0.013

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.%(*)
32444	125.230	766.2607	11.6500	11.6526	0.869	0.869	0.022	0.056
32422	110.030	871.9045	8.9100	8.7733	0.860	0.847	-1.534	-1.158
32411	100.020	979.5176	7.0100	6.9662	0.837	0.831	-0.625	0.347
32072	120.030	1020.0886	8.6200	8.6032	0.893	0.891	-0.195	-0.107
32063	125.230	1142.9917	8.1900	8.1876	0.911	0.911	-0.029	0.011
32062	120.030	1300.4656	6.9400	6.9214	0.916	0.914	-0.267	-0.192
32053	125.230	1452.0801	6.5800	6.5759	0.930	0.929	-0.063	-0.025
32052	120.030	1618.2141	5.6600	5.6631	0.930	0.930	0.054	0.118
32042	120.030	1917.8225	4.8400	4.8332	0.942	0.941	-0.141	-0.085
32043	125.230	1986.7737	4.9000	4.9028	0.947	0.948	0.058	0.091
32165	126.190	2108.5879	4.6600	4.6733	0.949	0.952	0.286	0.315
32033	125.230	2222.0916	4.4000	4.4087	0.951	0.953	0.198	0.229
32032	120.030	2369.2944	3.9500	3.9582	0.950	0.952	0.207	0.255
32022	120.030	2591.0015	3.6400	3.6348	0.958	0.956	-0.142	-0.098
32421	100.020	2597.8523	2.9700	2.9550	0.940	0.935	-0.505	-0.163
32023	125.230	2707.5750	3.6500	3.6495	0.962	0.962	-0.013	0.014
32432	110.030	4490.3203	1.9500	1.9494	0.970	0.969	-0.033	0.041
32012	120.030	4729.8945	2.0300	2.0321	0.975	0.976	0.104	0.130
32013	125.230	4976.5547	2.0200	2.0215	0.978	0.979	0.074	0.091
32431	100.020	7905.2734	1.0200	1.0160	0.982	0.979	-0.390	-0.280

391 NO.OF DATA POINTS : 50. AVG.DEV.% : 0.171 0.157

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
34176	133.150	208.3358	33.0900	33.1263	0.631	0.632	0.110	-0.147
33146	143.150	279.7856	31.6128	31.6650	0.753	0.754	0.165	-0.052
34166	133.150	285.9277	27.3700	27.3994	0.716	0.717	0.108	-0.109
34167	143.140	297.9980	30.1900	30.2332	0.766	0.767	0.143	-0.051
34156	133.150	312.5583	25.7800	25.7993	0.737	0.738	0.075	-0.115
33136	143.150	326.8748	28.1751	28.2080	0.784	0.785	0.117	-0.043
34157	143.140	327.5989	28.1200	28.1573	0.784	0.785	0.133	-0.026
34617	158.150	347.4692	31.2700	31.2623	0.837	0.837	-0.025	-0.029
33137	163.150	352.4727	32.3173	32.2982	0.851	0.850	-0.059	-0.015
32066	150.040	391.5605	26.2400	26.2428	0.834	0.835	0.011	-0.035
34146	133.150	428.9717	20.4300	20.4377	0.802	0.802	0.038	-0.058
34147	143.140	447.1021	21.9800	21.9925	0.837	0.837	0.057	-0.004
33126	143.150	447.2285	21.9791	21.9895	0.837	0.837	0.048	-0.013
34136	133.150	468.9326	19.0600	19.0550	0.818	0.818	-0.026	-0.100
34607	158.150	467.6428	24.2900	24.2699	0.875	0.875	-0.083	-0.024
34137	143.140	491.5234	20.3200	20.3259	0.850	0.851	0.029	-0.009
33127	163.150	502.7837	23.7288	23.7134	0.891	0.891	-0.065	0.037
33138	203.150	503.1226	31.1468	31.0969	0.940	0.939	-0.160	0.041
34148	183.150	510.3835	27.0600	27.0504	0.919	0.919	-0.036	0.156
33116	143.150	522.4885	19.3033	19.3059	0.859	0.859	0.013	-0.012
34597	158.150	520.8147	22.1000	22.0817	0.887	0.886	-0.083	-0.010
33117	163.150	563.3596	21.4417	21.4184	0.902	0.901	-0.109	0.002
34138	183.150	578.7256	24.1000	24.0801	0.928	0.927	-0.082	0.107
33128	203.150	581.5847	27.1471	27.1102	0.947	0.946	-0.136	0.060
34149	223.130	581.6257	30.2700	30.2378	0.962	0.961	-0.106	0.040
34126	133.150	643.5776	14.6800	14.6710	0.865	0.864	-0.061	-0.079
34139	223.130	663.9985	26.6300	26.6038	0.966	0.965	-0.098	0.043
34127	143.140	670.8184	15.5500	15.5473	0.888	0.888	-0.017	-0.005
34649	273.150	680.6887	32.5600	32.5624	0.989	0.989	0.007	-0.078
34116	133.150	703.5293	13.6000	13.5903	0.876	0.875	-0.071	-0.078

Region IIa

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
33106	143.150	714.6345	14.7013	14.7015	0.894	0.894	0.001	0.020
32056	150.040	712.2297	15.6400	15.6311	0.905	0.904	-0.057	-0.005
34587	158.150	700.9692	16.9300	16.9105	0.914	0.913	-0.115	-0.022
33129	273.150	727.3086	30.4770	30.4908	0.989	0.989	0.045	-0.032
34117	143.140	737.4756	14.2900	14.2940	0.897	0.897	0.028	0.049
34128	183.150	765.1406	18.5400	18.5346	0.944	0.944	-0.029	0.146
34577	158.150	780.6716	15.3400	15.3220	0.923	0.922	-0.118	-0.022
34639	273.150	784.1516	28.3000	28.2967	0.990	0.990	-0.012	-0.081
33107	163.150	803.4565	15.4915	15.4785	0.930	0.929	-0.084	0.033
33118	203.150	802.0208	19.9714	19.9412	0.961	0.959	-0.151	0.021
32449	299.990	819.4827	29.9600	29.9802	0.997	0.998	0.067	-0.123
33096	143.150	834.9097	12.7894	12.7866	0.909	0.909	-0.022	0.008
34118	183.150	867.6035	16.4600	16.4533	0.950	0.950	-0.041	0.124
34129	223.130	872.0237	20.4300	20.4163	0.973	0.972	-0.067	0.060
33097	163.150	900.2166	13.9350	13.9221	0.937	0.936	-0.092	0.021
33108	203.150	927.0837	17.3632	17.3423	0.966	0.964	-0.120	0.039
34106	133.150	965.5466	10.2800	10.2700	0.908	0.908	-0.098	-0.081
34119	223.130	995.5176	17.9600	17.9415	0.976	0.975	-0.103	0.015
34107	143.140	1006.4875	10.7800	10.7795	0.924	0.924	-0.005	0.033
33119	273.150	1006.4297	22.0770	22.0867	0.991	0.992	0.044	-0.004
34629	273.150	1020.6787	21.7800	21.7804	0.992	0.992	0.002	-0.045
34096	133.150	1055.4998	9.4800	9.4732	0.916	0.915	-0.072	-0.052
34567	158.150	1050.7090	11.6300	11.6212	0.942	0.941	-0.076	0.016
34097	143.140	1106.5007	9.8800	9.8755	0.931	0.930	-0.045	-0.006
33086	143.150	1141.6497	9.5933	9.5935	0.932	0.932	0.002	0.042
32046	150.040	1144.0017	10.1100	10.1049	0.939	0.939	-0.050	0.012
34108	183.150	1147.0715	12.6000	12.5967	0.962	0.961	-0.026	0.115
33109	273.150	1157.9897	19.2075	19.2135	0.992	0.993	0.031	-0.008
34557	158.150	1170.1826	10.5100	10.4989	0.948	0.947	-0.106	-0.018
34619	273.150	1175.8325	18.9300	18.9237	0.993	0.993	-0.033	-0.072

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
32057	175.020	1261.6646	10.9500	10.9352	0.962	0.961	-0.135	-0.012
33098	203.150	1278.3596	12.7084	12.6974	0.975	0.974	-0.086	0.043
33087	163.150	1283.7097	9.9596	9.9542	0.955	0.954	-0.054	0.044
34098	183.150	1300.6655	11.1600	11.1595	0.966	0.966	-0.005	0.125
34109	223.130	1307.4365	13.7400	13.7378	0.981	0.981	-0.016	0.083
33076	143.150	1333.8596	8.2962	8.2941	0.942	0.942	-0.026	0.015
33077	163.150	1438.2595	8.9366	8.9285	0.960	0.959	-0.091	0.001
34086	133.150	1448.6099	7.0800	7.0713	0.939	0.938	-0.123	-0.097
33088	203.150	1477.6997	11.0330	11.0228	0.978	0.977	-0.093	0.023
34099	223.130	1492.5806	12.0700	12.0611	0.984	0.983	-0.073	0.016
34087	143.140	1510.1206	7.3800	7.3767	0.949	0.948	-0.044	-0.004
34609	273.150	1530.5120	14.5600	14.5602	0.994	0.994	0.001	-0.026
34547	158.150	1574.9431	7.9200	7.9101	0.961	0.960	-0.125	-0.050
34076	133.150	1583.5537	6.5100	6.5045	0.944	0.943	-0.084	-0.058
33099	273.150	1602.2993	13.9070	13.9111	0.994	0.994	0.029	0.004
34077	143.140	1660.1860	6.7400	6.7421	0.953	0.953	0.031	0.070
32036	150.040	1715.1870	6.8900	6.8819	0.960	0.959	-0.117	-0.063
34088	183.150	1719.6467	8.5100	8.5110	0.974	0.974	0.011	0.117
34527	158.150	1754.0076	7.1400	7.1320	0.965	0.964	-0.112	-0.042
34599	273.150	1763.1570	12.6500	12.6477	0.995	0.995	-0.018	-0.040
33066	143.150	1823.5088	6.1636	6.1652	0.957	0.957	0.026	0.064
33089	273.150	1843.6897	12.0988	12.0977	0.995	0.995	-0.009	-0.030
32047	175.020	1862.6716	7.5100	7.5019	0.974	0.973	-0.108	-0.014
34078	183.150	1949.9136	7.5300	7.5290	0.977	0.977	-0.013	0.083
34089	223.130	1960.2341	9.2200	9.2196	0.987	0.987	-0.004	0.068
33078	203.150	2037.4590	8.0497	8.0442	0.984	0.983	-0.068	0.022
33067	163.150	2050.7893	6.3411	6.3394	0.971	0.971	-0.027	0.045
33056	143.150	2130.6592	5.3104	5.3099	0.963	0.963	-0.010	0.025
34066	133.150	2173.3198	4.8200	4.8161	0.959	0.958	-0.081	-0.057
34079	223.130	2237.8413	8.0900	8.0886	0.989	0.989	-0.017	0.048

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
34067	143.140	2265.7927	5.0000	5.0040	0.964	0.965	0.080	0.114
34589	273.150	2295.0034	9.7300	9.7274	0.996	0.996	-0.026	-0.042
33057	163.150	2297.6389	5.6765	5.6760	0.975	0.974	-0.044	0.022
33068	203.150	2355.1792	6.9796	6.9747	0.986	0.985	-0.071	0.009
34527	158.150	2360.7349	5.3500	5.3489	0.973	0.973	-0.020	0.037
34056	133.150	2375.7947	4.4200	4.4219	0.961	0.961	0.042	0.065
34057	143.140	2490.9189	4.5700	4.5663	0.969	0.968	-0.081	-0.049
32026	150.040	2553.8801	4.6900	4.6861	0.973	0.972	-0.083	-0.041
33079	273.150	2550.9587	8.7531	8.7547	0.996	0.996	0.019	0.005
34068	183.150	2578.0410	5.7300	5.7268	0.983	0.982	-0.056	0.020
34517	158.150	2629.1829	4.8200	4.8161	0.976	0.976	-0.080	-0.028
34579	273.150	2643.8330	8.4500	8.4482	0.997	0.996	-0.021	-0.035
33046	143.150	2912.3389	3.9228	3.9240	0.973	0.973	0.031	0.060
34058	183.150	2923.2715	5.0600	5.0610	0.984	0.984	0.019	0.087
34069	223.130	2939.0117	6.1800	6.1754	0.992	0.991	-0.075	-0.024
33069	273.150	2935.3586	7.6124	7.6117	0.997	0.997	-0.009	-0.021
32459	299.990	3029.8911	8.1100	8.1171	0.998	0.999	0.087	0.037
32037	175.020	3088.2659	4.5800	4.5738	0.985	0.983	-0.136	-0.075
33058	203.150	3247.1685	5.0811	5.0789	0.990	0.989	-0.043	0.018
34046	133.150	3260.6006	3.2600	3.2565	0.973	0.972	-0.107	-0.088
33047	163.150	3275.9888	4.0129	4.0120	0.982	0.982	-0.022	0.027
34059	223.130	3355.2334	5.4200	5.4151	0.993	0.992	-0.090	-0.045
34047	143.140	3399.6343	3.3800	3.3746	0.978	0.977	-0.160	-0.134
33036	143.150	3403.1387	3.3712	3.3714	0.977	0.977	0.007	0.033
34569	273.150	3441.3958	6.5000	6.4953	0.998	0.997	-0.072	-0.081
34036	133.150	3564.3691	2.9900	2.9863	0.975	0.974	-0.125	-0.107
33037	163.150	3670.2493	3.5893	3.5881	0.984	0.984	-0.033	0.012
34037	143.140	3737.4036	3.0800	3.0761	0.980	0.979	-0.125	-0.101
33048	203.150	3753.5383	4.4019	4.4001	0.991	0.991	-0.042	0.011
34048	183.150	3864.9769	3.8400	3.8424	0.988	0.988	0.063	0.116

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
32058	200.110	3891.4475	4.1800	4.1803	0.991	0.991	0.008	0.060
34559	273.150	3964.4695	5.6400	5.6403	0.998	0.998	0.006	-0.003
33059	273.150	4061.2292	5.5054	5.5062	0.998	0.998	0.015	0.007
34038	183.150	4382.5586	3.3900	3.3934	0.989	0.990	0.100	0.147
34049	223.130	4406.5078	4.1300	4.1307	0.994	0.994	0.017	0.053
32048	200.110	4496.4492	3.6200	3.6224	0.991	0.992	0.066	0.111
33026	143.150	4650.9844	2.4810	2.4825	0.982	0.983	0.061	0.081
33049	273.150	4673.3945	4.7869	4.7864	0.998	0.998	-0.011	-0.017
34026	133.150	4891.8398	2.1900	2.1914	0.980	0.981	0.065	0.079
34039	223.130	5030.5938	3.6200	3.6209	0.995	0.995	0.024	0.056
34027	143.140	5100.6758	2.2700	2.2669	0.986	0.984	-0.136	-0.117
34549	273.150	5160.3477	4.3400	4.3355	0.999	0.998	-0.103	-0.109
33038	203.150	5175.0352	3.2009	3.1995	0.994	0.993	-0.043	-0.003
33027	163.150	5232.8828	2.5286	2.5290	0.988	0.988	0.016	0.048
34016	133.150	5347.7031	2.0100	2.0079	0.984	0.983	-0.106	-0.093
33016	143.150	5435.1953	2.1287	2.1296	0.985	0.985	0.042	0.060
34017	143.140	5607.5313	2.0700	2.0649	0.988	0.986	-0.244	-0.227
32016	150.040	5700.2148	2.1300	2.1326	0.986	0.987	0.122	0.144
34028	183.150	5794.1758	2.5700	2.5732	0.991	0.992	0.125	0.162
33017	163.150	5862.5859	2.2596	2.2602	0.989	0.990	0.024	0.054
34539	273.150	5944.8398	3.7600	3.7643	0.997	0.998	0.115	0.110
33028	203.150	5982.0547	2.7715	2.7704	0.995	0.994	-0.039	-0.005
33039	273.150	6465.5352	3.4616	3.4616	0.999	0.999	0.000	-0.005
34018	183.150	6570.2578	2.2700	2.2714	0.992	0.993	0.062	0.094
34029	223.130	6606.6680	2.7600	2.7605	0.996	0.996	0.017	0.041
32027	175.020	6685.2930	2.1300	2.1318	0.991	0.992	0.083	0.114
33029	273.150	7440.5156	3.0090	3.0086	0.999	0.999	-0.014	-0.018
34019	223.130	7542.3945	2.4200	2.4192	0.997	0.997	-0.034	-0.012
32038	200.110	7711.0195	2.1200	2.1194	0.996	0.995	-0.028	-0.000
34529	273.150	7737.9688	2.8900	2.8931	0.998	0.999	0.106	0.102

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
33018	203.150	8247.5039	2.0131	2.0127	0.996	0.996	-0.022	0.003
34519	273.150	8914.2734	2.5100	2.5117	0.998	0.999	0.068	0.065
32028	200.110	10069.6953	1.6200	1.6248	0.993	0.996	0.295	0.316
33019	273.150	10293.2930	2.1759	2.1755	0.999	0.999	-0.017	-0.020
32469	299.990	11944.1523	2.0600	2.0605	1.000	1.000	0.023	0.010
32017	175.020	12441.2305	1.1500	1.1496	0.996	0.996	-0.035	-0.018
32018	200.110	14261.9141	1.1500	1.1484	0.999	0.997	-0.138	-0.123

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NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
34216	133.150	92.5625	44.5400	44.5550	0.377	0.377	0.034	0.304
34687	158.150	92.6425	84.5400	84.0919	0.603	0.600	-0.530	0.146
34217	143.140	96.9926	58.9000	58.8221	0.486	0.486	-0.132	0.370
33219	273.150	98.4028	245.0780	245.2168	1.076	1.077	0.057	0.125
34228	183.150	101.0527	113.6500	113.1502	0.764	0.761	-0.440	0.148
34677	158.150	103.1828	77.5399	77.2858	0.617	0.614	-0.328	0.143
34739	273.150	103.4728	230.4300	230.2669	1.064	1.063	-0.071	-0.102
35116	128.000	105.5899	36.0296	35.9168	0.362	0.361	-0.313	-0.042
35117	130.000	105.6695	38.7427	38.6262	0.384	0.383	-0.301	0.004
35167	132.000	105.7493	41.4310	41.3192	0.404	0.403	-0.270	0.054
35118	134.000	105.8292	44.1017	43.9967	0.424	0.423	-0.238	0.099
35168	136.000	105.9093	46.7555	46.6593	0.444	0.443	-0.206	0.139
35119	138.000	105.9893	49.4014	49.3082	0.462	0.462	-0.189	0.161
35169	140.000	106.0295	52.0336	51.9525	0.480	0.479	-0.156	0.198
33186	143.150	109.3529	55.2750	55.2340	0.515	0.514	-0.074	0.235
33209	273.150	113.1869	206.1180	206.6824	1.041	1.044	0.274	0.060
34218	183.150	114.5831	100.8100	100.5935	0.769	0.767	-0.215	0.141
34229	223.130	115.1231	146.0700	145.7479	0.918	0.916	-0.221	0.017
33187	163.150	122.9900	73.4934	73.4399	0.675	0.675	-0.073	0.090
33198	203.150	124.0989	114.3900	114.2224	0.852	0.850	-0.147	0.080
34206	133.150	127.0336	40.7400	40.6666	0.474	0.473	-0.180	0.001
33176	143.150	127.7700	51.0653	51.0670	0.555	0.555	0.003	0.047
32419	299.990	130.1840	200.3700	201.6714	1.060	1.067	0.650	-0.109
34219	223.130	131.4236	127.0200	126.9623	0.912	0.911	-0.045	0.019
34207	143.140	132.3736	50.1300	50.1455	0.565	0.565	0.031	0.021
34729	273.150	134.6738	168.9600	169.4890	1.015	1.018	0.313	-0.145
33177	163.150	137.8409	67.5019	67.5049	0.695	0.695	0.005	0.020
34196	133.150	138.8639	39.5600	39.5168	0.503	0.502	-0.109	-0.048
34667	158.150	138.8639	62.6300	62.6405	0.670	0.670	0.017	-0.011
33188	203.150	143.4559	99.4314	99.4398	0.856	0.856	0.009	0.107

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
34197	143.140	145.5240	47.6800	47.7340	0.591	0.591	0.113	-0.020
34208	183.150	151.4941	78.7400	78.8079	0.794	0.794	0.086	0.151
34657	158.150	154.6543	58.0500	58.1106	0.692	0.692	0.104	-0.011
34719	273.150	155.1342	144.7200	145.2344	1.002	1.005	0.355	-0.170
33199	273.150	155.6319	143.0060	143.7430	0.999	1.004	0.515	-0.012
34198	183.150	171.7747	70.7200	70.7903	0.808	0.809	0.099	0.137
34209	223.130	172.5947	96.7800	96.8452	0.912	0.913	0.067	0.036
33166	143.150	174.9539	43.0028	43.0918	0.640	0.642	0.207	-0.064
[illegible]	273.150	180.1899	123.3100	123.8973	0.991	0.996	0.476	-0.034
34186	133.150	190.5853	34.6300	34.6706	0.604	0.605	0.117	-0.116
33167	163.150	196.7199	51.6873	51.7502	0.759	0.760	0.122	0.011
33178	203.150	197.9050	73.8141	73.8117	0.876	0.876	-0.003	0.072
34199	223.130	197.0355	85.1700	85.1958	0.917	0.917	0.030	0.022
34187	143.140	198.6156	39.8100	39.9075	0.673	0.675	0.245	-0.052
34709	273.150	201.9155	109.7200	110.0541	0.988	0.991	0.305	-0.163
33156	143.150	204.4120	39.1127	39.1981	0.681	0.682	0.218	-0.078
34647	158.150	208.1458	46.8400	46.8835	0.751	0.752	0.093	-0.063
34177	143.140	218.3461	37.4800	37.5645	0.697	0.698	0.226	-0.064
33157	163.150	220.4599	47.3504	47.3791	0.780	0.780	0.061	-0.028
32429	299.990	223.0559	111.7800	112.0566	1.013	1.015	0.247	-0.472
34188	183.150	227.0959	55.6900	55.7276	0.841	0.842	0.068	0.144
33168	203.150	228.7779	64.6283	64.6261	0.887	0.887	-0.003	0.105
34637	158.150	231.8065	43.1700	43.2168	0.771	0.772	0.108	-0.023
34699	273.150	232.5965	94.9600	95.1849	0.985	0.988	0.237	-0.165
33179	273.150	249.3830	88.3856	88.6743	0.983	0.987	0.327	-0.043
34178	183.150	257.5066	49.9600	49.9715	0.856	0.856	0.023	0.131
34189	223.130	258.7568	65.6600	65.6417	0.928	0.928	-0.028	0.037
34179	223.130	295.3979	57.9000	57.8595	0.934	0.933	-0.070	0.026
34689	273.150	302.7581	72.8200	72.9232	0.984	0.985	0.142	-0.143
34627	158.150	311.9878	34.1700	34.1637	0.821	0.821	-0.018	-0.055

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
33147	163.150	314.5527	35.5412	35.5443	0.835	0.835	0.009	0.024
33158	203.150	315.5728	48.1322	48.0749	0.911	0.910	-0.119	0.055
34168	183.150	340.4497	39.0500	39.0620	0.885	0.885	0.031	0.194
34679	273.150	348.7595	63.2300	63.2968	0.984	0.985	0.106	-0.126
33148	203.150	364.7947	42.0765	42.0284	0.921	0.920	-0.114	0.077
34158	183.150	386.0405	34.9200	34.8958	0.897	0.896	-0.069	0.109
33169	273.150	286.9067	76.7758	76.9715	0.983	0.985	0.255	-0.052
34169	223.130	387.9407	44.6500	44.6126	0.946	0.945	-0.084	0.052
33159	273.150	397.0427	55.5286	55.6206	0.984	0.985	0.166	-0.026
34159	223.130	442.8716	39.3400	39.3007	0.952	0.951	-0.100	0.044
34669	273.150	453.9524	48.6600	48.6821	0.985	0.986	0.045	-0.111
33149	273.150	456.7986	48.3237	48.3806	0.985	0.986	0.118	-0.037
32439	299.990	489.2036	50.1700	50.2781	0.997	0.999	0.216	-0.112
34659	273.150	522.9543	42.2900	42.2990	0.987	0.987	0.021	-0.105
33139	273.150	632.1377	35.0144	35.0432	0.987	0.988	0.082	-0.013

391 NO.OF DATA POINTS : 75. AVG.DEV.% : 0.158 0.093

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
30CC5	126.200	90.1000	33.5000	33.4998	0.291	0.291	-0.000	-0.569
33208	203.150	89.9706	161.5620	160.4173	0.872	0.866	-0.709	0.023
34749	273.150	89.8325	277.1797	276.4678	1.111	1.108	-0.257	-0.062
35216	128.000	88.7611	36.5132	36.5178	0.309	0.309	0.013	-0.322
35226	128.000	88.7049	36.5191	36.5202	0.308	0.308	0.003	-0.334
35217	130.000	88.8174	39.8243	39.8679	0.332	0.332	0.109	0.047
35227	130.000	88.7611	39.8401	39.8730	0.331	0.332	0.083	0.018
35267	132.000	88.9019	43.1582	43.2098	0.354	0.355	0.120	0.256
35277	132.000	88.8455	43.1789	43.2176	0.354	0.354	0.090	0.225
35218	134.000	88.5584	46.5068	46.5498	0.376	0.377	0.093	0.376
35228	134.000	88.9019	46.5216	46.5605	0.376	0.376	0.084	0.366
35268	136.000	89.0432	49.8485	49.8780	0.398	0.398	0.059	0.451
35278	136.000	88.9584	49.8722	49.8985	0.398	0.398	0.053	0.444
35219	138.000	89.0999	53.1942	53.2070	0.419	0.419	0.024	0.497
35229	138.000	89.0432	53.2277	53.2235	0.419	0.418	-0.008	0.465
35269	140.000	89.1566	56.5428	56.5308	0.439	0.439	-0.021	0.513
35279	140.000	89.0999	56.5813	56.5503	0.439	0.439	-0.055	0.479
34227	143.140	88.2325	62.2400	62.1780	0.468	0.467	-0.100	0.512
34239	223.130	87.6725	201.3300	199.8603	0.964	0.957	-0.730	-0.082
33197	163.150	86.1828	99.0350	98.3447	0.638	0.633	-0.697	0.082
34226	133.150	84.6724	45.7900	45.9151	0.355	0.356	0.273	0.441
33196	143.150	79.8490	66.6651	66.6532	0.453	0.453	-0.018	0.635
33207	163.150	76.9059	111.8840	111.0904	0.643	0.638	-0.709	0.009
34238	183.150	76.4421	156.3300	155.1704	0.795	0.789	-0.742	-0.103
33218	203.150	77.8542	194.8920	193.4611	0.910	0.904	-0.734	-0.126
34249	223.130	76.8022	241.8300	240.4132	1.014	1.008	-0.586	-0.150
33229	273.150	71.1195	393.3228	396.7344	1.248	1.259	0.867	0.336
31335	126.201	69.9760	33.9650	33.9761	0.230	0.230	0.033	-1.311
31336	129.993	70.0350	42.8070	43.0771	0.281	0.283	0.631	0.313
31337	135.011	70.0990	54.9430	55.2346	0.348	0.349	0.531	0.791

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
31338	139.995	70.1600	67.2580	67.4077	0.411	0.412	0.223	0.686
33206	143.150	68.3585	77.4796	77.5573	0.451	0.451	0.100	0.536
34697	158.150	68.8419	116.3900	115.7797	0.617	0.614	-0.524	-0.179
34759	273.150	69.0319	415.0295	418.6245	1.278	1.289	0.866	0.072
34248	183.150	67.4219	188.5400	188.0672	0.846	0.844	-0.251	-0.291
34237	143.140	64.6518	83.5400	83.7255	0.460	0.461	0.222	0.448
31325	126.199	62.3470	36.2400	36.2534	0.218	0.218	0.037	-0.251
31326	130.003	62.3980	47.5639	47.8246	0.278	0.280	0.548	0.676
31327	135.004	62.4690	62.8340	63.1504	0.354	0.356	0.504	0.722
31328	139.996	62.5330	78.3090	78.5559	0.426	0.428	0.315	0.454
34236	133.150	61.6917	58.2900	58.5321	0.329	0.330	0.415	0.636
34707	158.150	61.8117	139.2500	138.9882	0.663	0.662	-0.188	-0.591
33239	273.150	61.8397	506.0396	520.0854	1.396	1.435	2.776	0.658
35316	128.000	60.0364	43.8687	44.0344	0.251	0.252	0.378	0.650
35367	132.000	60.1525	56.8971	57.2535	0.316	0.318	0.627	0.874
35318	134.000	60.2042	63.4552	63.8786	0.347	0.350	0.667	0.858
35368	136.000	60.2689	70.0360	70.4760	0.378	0.381	0.628	0.751
35319	138.000	60.3338	76.6297	77.0670	0.408	0.411	0.571	0.622
35369	140.000	60.3859	83.2243	83.6840	0.437	0.440	0.552	0.530

391 NO.OF CATA POINTS : 49. AVG.DEV.% : 0.384 0.425

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
34247	143.140	58.8116	99.2800	99.6565	0.497	0.499	0.379	0.070
34259	223.130	58.5016	392.2498	399.1365	1.253	1.275	1.756	-0.246
34769	273.150	59.9417	541.0696	556.1746	1.447	1.487	2.792	0.245
34246	133.150	56.4416	70.2700	70.3142	0.363	0.363	0.063	0.176
33228	203.150	56.5122	345.0796	351.3472	1.170	1.191	1.816	-0.227
31225	126.206	54.8950	47.1519	46.8366	0.250	0.248	-0.669	0.324
31226	130.004	54.9420	62.6440	62.5651	0.323	0.322	-0.126	0.274
31227	134.999	55.0140	83.1950	83.2392	0.413	0.413	0.053	-0.093
31228	140.027	55.0650	103.9310	104.1580	0.498	0.499	0.218	-0.318
35416	128.000	53.6339	58.6805	58.7220	0.300	0.300	0.071	0.759
35417	130.000	53.6956	67.1710	67.3643	0.338	0.339	0.288	0.647
35467	132.000	53.7574	75.6615	75.9764	0.375	0.377	0.416	0.504
35418	134.000	53.8091	84.1224	84.6100	0.412	0.414	0.580	0.440
35468	136.000	53.8712	92.5645	93.1627	0.447	0.450	0.646	0.314
35419	138.000	53.9334	100.9386	101.6839	0.481	0.484	0.738	0.240
35469	140.000	53.9958	109.3412	110.1717	0.514	0.518	0.760	0.117
33217	163.150	53.9871	212.0950	213.4912	0.855	0.861	0.658	-0.934
33216	143.150	50.0133	159.6060	160.3084	0.680	0.683	0.440	-0.614
34258	183.150	51.0114	347.9757	354.6748	1.181	1.204	1.924	-0.308
34269	223.130	51.2514	536.2395	553.4980	1.501	1.549	3.218	0.066

391 NO.OF DATA POINTS : 20. AVG.DEV.% : 0.881 0.346

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
31315	126.202	49.7020	71.5520	71.5575	0.343	0.343	0.008	0.782
31316	130.003	49.7460	91.4990	91.9137	0.427	0.429	0.453	0.529
31317	135.022	49.8010	117.9250	118.6966	0.530	0.534	0.654	0.151
31318	140.014	49.8610	143.9880	145.1432	0.625	0.630	0.802	-0.078
33227	163.150	48.2368	299.5366	302.1360	1.079	1.089	0.868	-0.683
33238	203.150	48.9412	501.0337	514.7107	1.471	1.511	2.730	0.112
31215	126.198	44.9710	130.3190	130.7769	0.566	0.568	0.351	0.472
31216	130.010	45.0170	156.3800	156.8588	0.660	0.662	0.306	0.258
31217	135.037	45.0720	190.4419	191.0101	0.775	0.777	0.298	0.103
34717	158.150	45.9413	325.6997	326.4121	1.153	1.156	0.219	-0.649
34268	183.150	45.0013	519.6897	526.5835	1.556	1.577	1.327	0.328
34257	143.140	43.1112	306.0696	305.9568	1.123	1.123	-0.037	0.420
33226	143.150	42.9370	314.6545	312.1880	1.150	1.141	-0.784	-0.244
34256	133.150	41.1412	303.4597	301.2900	1.143	1.134	-0.715	0.268
34727	158.150	41.2712	517.7197	507.5479	1.646	1.614	-1.965	-0.100

391 NO.OF DATA POINTS : 15. AVG.DEV.% : 0.768 0.345

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
32035	126.190	81.1420	33.5100	33.4975	0.263	0.262	-0.037	-1.243
32025	126.190	69.7820	33.9000	33.9729	0.228	0.229	0.215	-1.123
32015	126.190	65.9920	34.5300	34.6920	0.220	0.221	0.469	-0.465
35315	126.000	59.9722	37.4409	37.4395	0.217	0.217	-0.004	0.184
35364	124.000	59.9209	31.1363	30.8412	0.183	0.182	-0.948	-0.991
31224	121.998	54.8420	30.3420	29.4570	0.166	0.161	-2.917	-0.922
35415	126.000	53.5724	50.1910	50.0520	0.260	0.259	-0.277	0.824
35464	124.000	53.5110	41.7468	41.3540	0.220	0.217	-0.941	0.696
35414	122.000	53.4497	33.3106	32.6297	0.178	0.174	-2.044	0.331
35413	120.000	53.3988	24.9524	23.8580	0.135	0.129	-4.386	-0.907
31314	122.002	49.6450	49.5770	49.0203	0.246	0.243	-1.123	1.009
36514	120.230	50.7700	34.5300	33.5381	0.178	0.173	-2.872	0.581
31313	117.997	49.5860	28.7390	27.4353	0.147	0.140	-4.536	0.609
36524	120.230	48.7100	47.5000	45.4613	0.235	0.224	-4.292	-1.664
36014	114.900	48.1300	20.5800	18.1497	0.105	0.093	-11.809	-2.972
36534	120.230	46.5600	67.6400	65.6557	0.319	0.310	-2.934	-1.447
36024	114.900	46.4600	34.1900	31.6939	0.168	0.156	-7.301	-2.629
31214	122.004	44.9200	101.4610	101.7749	0.455	0.457	0.309	0.729
36544	120.230	44.3100	101.6300	100.0949	0.456	0.450	-1.510	-1.193
31213	118.022	44.8720	73.8850	73.8889	0.342	0.342	0.005	0.957
36034	114.900	45.3000	47.6300	45.1700	0.229	0.217	-5.165	-2.696
31212	114.073	44.8220	46.4290	45.8989	0.222	0.220	-1.139	1.002
31211	110.269	44.7580	20.0360	18.7428	0.099	0.093	-6.454	-0.147
36513	110.000	44.9200	17.0100	14.6780	0.085	0.073	-13.709	-5.477
36523	110.000	44.1600	27.2900	25.2219	0.134	0.123	-7.578	-4.735

391 NO.OF DATA POINTS : 25. AVG.DEV.% : 3.319 1.421

ALL DATA HAVE BEEN PROCESSED

STOP 0
EXECUTION TERMINATED

APPENDIX II.1a

ARGON-NITROGEN

79.85% Ar - 20.15% N_2

48) Crain-Sonntag-Van Wylen data (26)

(*) The Benedict-Webb-Rubin equation with the constants in Table VI and the combining rule listed in Table V.

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
48166	143.150	154.4829	39.0898	38.9884	0.514	0.513	-0.259	-3.780
48156	143.150	201.4349	35.3929	35.3404	0.607	0.606	-0.148	-2.739
48146	143.150	247.2649	31.7846	31.7894	0.669	0.669	0.015	-2.060
48136	143.150	322.2966	26.9291	26.9153	0.739	0.738	-0.051	-1.611
48126	143.150	395.5217	23.2594	23.2569	0.783	0.783	-0.010	-1.265
48116	143.150	515.3816	18.9305	18.9296	0.831	0.831	-0.005	-0.950
48106	143.150	632.3625	15.9803	15.9824	0.860	0.860	0.013	-0.748
48096	143.150	823.8176	12.7109	12.7140	0.891	0.892	0.024	-0.550
48086	143.150	1010.6697	10.5853	10.5894	0.911	0.911	0.039	-0.423
48076	143.150	1316.4792	8.3051	8.3097	0.931	0.931	0.056	-0.293
48066	143.150	1614.9487	6.8604	6.8646	0.943	0.944	0.062	-0.218
48056	143.150	2103.4390	5.3384	5.3424	0.956	0.957	0.074	-0.136
48046	143.150	2580.1694	4.3878	4.3913	0.964	0.965	0.081	-0.087
48036	143.150	3360.5095	3.3979	3.4002	0.972	0.973	0.066	-0.058
48026	143.150	4121.9141	2.7840	2.7863	0.977	0.978	0.084	-0.015
48016	143.150	5368.4531	2.1492	2.1506	0.982	0.983	0.066	-0.006

84 NO.OF DATA POINTS : 16. AVG.DEV.% : 0.066 0.934

Region I

Region IIa

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
48147	163.150	253.9160	39.7700	39.7598	0.754	0.754	-0.026	-0.564
48137	163.150	306.8887	34.5386	34.5275	0.792	0.791	-0.032	-0.444
48127	163.150	405.4775	27.6781	27.6573	0.838	0.838	-0.075	-0.350
48138	203.150	420.8806	35.8107	35.7526	0.904	0.903	-0.162	0.119
48117	163.150	490.2737	23.5991	23.5851	0.864	0.864	-0.059	-0.268
48128	203.150	491.3958	31.1056	31.0505	0.917	0.915	-0.177	0.083
48139	273.150	546.5896	39.7200	39.6908	0.969	0.968	-0.073	-0.175
48107	163.150	647.2498	18.5220	18.5116	0.895	0.895	-0.056	-0.195
48118	203.150	670.9797	23.2961	23.2642	0.938	0.936	-0.137	0.077
48129	273.150	663.1106	32.9070	32.8827	0.974	0.973	-0.074	-0.154
48097	163.150	783.0017	15.6064	15.5997	0.913	0.912	-0.043	-0.148
48108	203.150	783.2297	20.1392	20.1128	0.946	0.945	-0.131	0.061
48119	273.150	870.1865	25.2234	25.2088	0.979	0.979	-0.058	-0.116
48087	163.150	1032.9297	12.0921	12.0908	0.933	0.933	-0.011	-0.080
48098	203.150	1069.5095	14.9638	14.9491	0.960	0.959	-0.098	0.054
48109	273.150	1055.7795	20.8640	20.8512	0.983	0.982	-0.062	-0.107
48077	163.150	1250.2195	10.1125	10.1109	0.944	0.944	-0.015	-0.067
48088	203.150	1248.2397	12.8949	12.8840	0.966	0.965	-0.084	0.051
48099	273.150	1385.3792	15.9620	15.9554	0.987	0.986	-0.041	-0.073
48067	163.150	1648.1194	7.7750	7.7771	0.957	0.957	0.026	-0.006
48078	203.150	1704.5091	9.5309	9.5247	0.975	0.974	-0.066	0.040
48089	273.150	1680.8989	13.1864	13.1813	0.989	0.988	-0.039	-0.063
48057	163.150	1995.9187	6.4707	6.4708	0.965	0.965	0.002	-0.021
48068	203.150	1989.0989	8.1973	8.1929	0.978	0.978	-0.054	0.040
48079	273.150	2205.5485	10.0752	10.0727	0.991	0.991	-0.025	-0.040
48047	163.150	2629.4294	4.9522	4.9545	0.973	0.973	0.047	0.035
48058	203.150	2716.6592	6.0373	6.0350	0.984	0.983	-0.038	0.036
48069	273.150	2676.1396	8.3162	8.3142	0.993	0.993	-0.025	-0.034
48037	163.150	3186.1392	4.1077	4.1084	0.978	0.978	0.017	0.010
48048	203.150	3169.5093	5.1869	5.1850	0.986	0.986	-0.037	0.029

NO.	T=K	V=CC/MOLE	PEXP=ATM.	PCAL=ATM.	Z	ZCAL	DEV.%	DEV.% (*)
48059	273.150	3511.2498	6.3495	6.3477	0.995	0.994	-0.029	-0.033
48027	163.150	4194.7930	3.1358	3.1375	0.983	0.983	0.053	0.052
48038	203.150	4329.3945	3.8111	3.8104	0.990	0.990	-0.019	0.034
48049	273.150	4260.6055	5.2375	5.2364	0.996	0.995	-0.022	-0.022
48017	163.150	5085.8438	2.5944	2.5955	0.986	0.986	0.044	0.046
48028	203.150	5050.2930	3.2720	3.2713	0.991	0.991	-0.020	0.027
48039	273.150	5589.8047	3.9965	3.9956	0.997	0.996	-0.023	-0.020
48018	203.150	6899.3828	2.4007	2.4003	0.994	0.993	-0.015	0.025
48029	273.150	6783.0859	3.2954	3.2947	0.997	0.997	-0.020	-0.015
48019	273.150	8898.1133	2.5137	2.5134	0.998	0.998	-0.014	-0.006

84 NO.OF DATA POINTS : 40. AVG.DEV.% : 0.051 0.095

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
48219	273.150	85.0648	253.1840	253.2589	0.961	0.961	0.030	0.799
48197	163.150	99.4141	68.4737	68.3891	0.508	0.508	-0.124	-1.262
48198	203.150	103.7310	117.0760	117.1946	0.729	0.729	0.101	0.916
48209	273.150	103.1700	203.3369	204.3460	0.936	0.941	0.496	0.500
48177	163.150	120.0590	62.5777	62.5796	0.561	0.561	0.003	-1.198
48188	203.150	121.1899	102.9580	103.1209	0.748	0.750	0.158	0.603
48199	273.150	135.4160	153.3620	154.2963	0.927	0.932	0.609	0.133
48167	163.150	158.9249	53.9211	53.9420	0.640	0.640	0.039	-0.935
48178	203.150	165.4870	79.8848	79.9663	0.793	0.794	0.102	0.381
48189	273.150	164.2759	126.7160	127.2720	0.929	0.933	0.439	-0.038
48157	163.150	192.0060	48.0704	48.0920	0.689	0.690	0.045	-0.737
48168	203.150	193.3020	70.3428	70.3175	0.816	0.815	-0.036	0.256
48179	273.150	215.6279	97.3894	97.5587	0.937	0.939	0.184	-0.172
48158	203.150	263.9636	54.0625	53.9981	0.856	0.855	-0.119	0.196
48169	273.150	261.5815	80.8893	80.9393	0.944	0.945	0.062	-0.210
48148	203.150	308.2595	47.2700	47.1839	0.874	0.872	-0.182	0.129
48159	273.150	343.3196	62.2839	62.2627	0.954	0.954	-0.034	-0.220
48149	273.150	416.4846	51.6939	51.6615	0.961	0.960	-0.063	-0.206

84 NO.OF DATA POINTS : 18. AVG.DEV.% : 0.157 0.494

Region IIb

NO_2	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
48197	163.150	75.0447	78.7746	78.6933	0.442	0.441	-0.103	-0.019
48208	203.150	75.9870	156.4630	155.4633	0.713	0.709	-0.639	1.648
48207	163.150	62.1869	90.8630	90.7296	0.422	0.421	-0.147	2.162
48218	203.150	65.0519	187.5210	186.8049	0.732	0.729	-0.382	2.194
48229	273.150	64.8188	364.3247	365.6951	1.054	1.058	0.376	1.013
48239	273.150	53.4615	506.5557	521.7925	1.208	1.245	3.008	0.582
48228	203.150	47.7400	328.0686	335.9482	0.940	0.962	2.402	1.138
48227	163.150	39.0859	311.5547	305.1714	0.910	0.891	-2.049	-1.455
48217	163.150	46.9843	149.1810	150.7735	0.524	0.529	1.068	4.735
48238	203.150	40.9148	510.3916	525.7451	1.253	1.290	3.008	-0.050

84 NO.OF DATA POINTS : 10. AVG.DEV.% : 1.318 1.500

APPENDIX II.1b

ARGON-NITROGEN

51.55% Ar - 48.45% N_2

45) Crain-Sonntag-Van Wylen data (26)

(*) The Benedict-Webb-Rubin equation with the constants in Table VI and the combining rule listed in Table V.

NO_2	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
45156	143.150	176.1859	39.2767	39.1332	0.589	0.587	-0.365	-1.394
45146	143.150	245.2139	32.8652	32.8221	0.686	0.685	-0.131	-0.870
45136	143.150	281.8767	30.0846	30.0415	0.722	0.721	-0.143	-0.777
45147	163.150	275.3367	38.2790	38.1547	0.787	0.785	-0.327	-0.207
45137	163.150	311.6135	34.7162	34.6488	0.808	0.806	-0.194	-0.067
45126	143.150	392.2046	23.7417	23.7287	0.793	0.792	-0.055	-0.487
45127	163.150	439.6296	26.1534	26.1160	0.859	0.858	-0.143	-0.009
45116	143.150	450.7026	21.3168	21.2973	0.818	0.817	-0.091	-0.457
45128	203.150	457.6746	33.4648	33.3993	0.919	0.917	-0.196	0.089
45117	163.150	497.3896	23.5167	23.4926	0.874	0.873	-0.102	0.030
45118	203.150	524.3635	29.5117	29.4527	0.928	0.926	-0.200	0.062
45149	273.150	572.1477	38.2052	38.1931	0.975	0.975	-0.032	-0.304
45106	143.150	627.0266	16.2208	16.2184	0.866	0.866	-0.015	-0.259
45139	273.150	680.2637	32.2474	32.2334	0.979	0.978	-0.043	-0.275
45107	163.150	701.7156	17.3214	17.3182	0.908	0.908	-0.018	0.101
45096	143.150	720.3557	14.3942	14.3873	0.883	0.882	-0.048	-0.253
45108	203.150	729.6426	21.6404	21.6046	0.947	0.946	-0.165	0.043
45097	163.150	793.6807	15.4822	15.4829	0.918	0.918	0.005	0.117
45098	203.150	835.8635	19.0179	18.9883	0.954	0.952	-0.155	0.033
45129	273.150	910.9456	24.1986	24.1908	0.983	0.983	-0.032	-0.207
45086	143.150	1002.1296	10.7152	10.7167	0.914	0.914	0.014	-0.122
45119	273.150	1083.0596	20.4051	20.3969	0.986	0.986	-0.040	-0.187
45076	143.150	1151.0396	9.4409	9.4401	0.925	0.925	-0.008	-0.122
45087	163.150	1119.7996	11.2438	11.2496	0.940	0.941	0.052	0.146
45088	203.150	1163.0596	13.8476	13.8310	0.966	0.965	-0.120	0.027
45077	163.150	1266.2097	10.0144	10.0188	0.947	0.948	0.044	0.131
45078	203.150	1332.2295	12.1410	12.1283	0.970	0.969	-0.105	0.027
45109	273.150	1450.3589	15.2884	15.2842	0.989	0.989	-0.027	-0.136
45066	143.150	1601.2886	6.9349	6.9371	0.945	0.946	0.032	-0.042
45099	273.150	1724.2996	12.8810	12.8775	0.991	0.991	-0.027	-0.117

Region IIa

NO.	T=K	V=CC/MOLE	PEXP=ATM.	PCAL=ATM.	Z	ZCAL	DEV.%	DEV.% (*)
45067	163.150	1786.7295	7.2047	7.2120	0.962	0.962	0.101	0.172
45056	143.150	1838.8694	6.0832	6.0849	0.952	0.953	0.028	-0.034
45068	203.150	1853.7388	8.7995	8.7919	0.978	0.978	-0.086	0.015
45057	163.150	2019.8396	6.4044	6.4078	0.966	0.967	0.053	0.118
45058	203.150	2123.1990	7.7026	7.6978	0.981	0.980	-0.062	0.029
45089	273.150	2309.1194	9.6396	9.6387	0.993	0.993	-0.015	-0.079
45046	143.150	2558.3591	4.4328	4.4341	0.965	0.966	0.029	-0.009
45079	273.150	2745.1389	8.1173	8.1162	0.994	0.994	-0.013	-0.066
45047	163.150	2850.6587	4.5816	4.5851	0.976	0.976	0.078	0.130
45036	143.150	2937.3887	3.8781	3.8794	0.970	0.970	0.034	0.003
45048	203.150	2954.4487	5.5657	5.5626	0.986	0.986	-0.056	0.015
45037	163.150	3221.7595	4.0661	4.0682	0.978	0.979	0.052	0.100
45038	203.150	3383.6995	4.8678	4.8656	0.988	0.988	-0.045	0.019
45069	273.150	3676.2896	6.0700	6.0695	0.996	0.995	-0.008	-0.044
45026	143.150	4087.1096	2.8101	2.8121	0.978	0.978	0.072	0.054
45059	273.150	4370.2734	5.1099	5.1093	0.996	0.996	-0.012	-0.039
45027	163.150	4547.7930	2.8989	2.8999	0.985	0.985	0.034	0.073
45016	143.150	4691.8242	2.4553	2.4566	0.981	0.981	0.052	0.039
45028	203.150	4708.4961	3.5103	3.5088	0.991	0.991	-0.042	0.009
45017	163.150	5138.5938	2.5694	2.5709	0.986	0.987	0.059	0.096
45018	203.150	5392.3750	3.0688	3.0673	0.993	0.992	-0.049	-0.002
45049	273.150	5852.8750	3.8192	3.8187	0.997	0.997	-0.013	-0.030
45039	273.150	6957.4336	3.2142	3.2139	0.998	0.998	-0.009	-0.021
45029	273.150	9318.0625	2.4018	2.4011	0.998	0.998	-0.027	-0.032
45019	273.150	11076.1953	2.0210	2.0206	0.999	0.998	-0.020	-0.022

90 NO.OF DATA POINTS : 55. AVG.DEV.% : 0.072 0.152

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
45186	143.150	95.6831	47.3041	46.6884	0.385	0.380	-1.301	-3.592
45229	273.150	89.0417	252.6910	252.5553	1.004	1.003	-0.054	0.729
45176	143.150	110.0589	45.9882	45.4793	0.431	0.426	-1.107	-2.909
45187	163.150	107.8419	71.3455	70.6958	0.575	0.569	-0.911	-0.124
45188	203.150	112.8129	114.5809	114.4206	0.775	0.774	-0.140	1.048
45219	273.150	105.9259	206.0829	206.6080	0.974	0.976	0.255	0.318
45177	163.150	122.1490	66.2477	65.7878	0.604	0.600	-0.694	-0.234
45178	203.150	129.3079	101.6040	101.5866	0.788	0.788	-0.017	0.790
45166	143.150	153.2199	41.6484	41.4379	0.543	0.540	-0.505	-1.683
45209	273.150	141.7419	150.6969	151.4899	0.953	0.958	0.526	-0.073
45167	163.150	172.3630	53.4928	53.2499	0.689	0.686	-0.454	-0.322
45168	203.150	179.9610	76.5412	76.4921	0.826	0.826	-0.064	0.396
45199	273.150	168.5979	126.4120	126.9002	0.951	0.955	0.386	-0.284
45157	163.150	195.1450	49.1656	49.0026	0.717	0.714	-0.332	-0.220
45158	203.150	206.2500	68.0841	68.0096	0.842	0.841	-0.109	0.308
45189	273.150	225.6839	94.6973	94.8955	0.953	0.955	0.209	-0.388
45179	273.150	268.3977	79.9534	80.0306	0.957	0.958	0.097	-0.429
45148	203.150	287.0276	51.0257	50.9205	0.879	0.877	-0.206	0.155
45138	203.150	329.8967	45.1898	45.0965	0.892	0.890	-0.206	0.133
45169	273.150	359.3325	60.1590	60.1715	0.964	0.965	0.021	-0.392
45159	273.150	427.2747	50.8195	50.8116	0.969	0.969	-0.015	-0.370

90 NO. OF DATA POINTS : 21. AVG. DEV.% : 0.362 0.709

Region IIb

NO_2	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
45198	203.150	81.0824	158.4360	157.0743	0.771	0.764	-0.859	1.892
45197	163.150	76.4435	89.7847	88.2321	0.513	0.504	-1.729	0.937
45196	143.150	68.7311	51.0252	50.3405	0.299	0.295	-1.342	-3.216
45207	163.150	67.4892	101.0910	98.9846	0.510	0.499	-2.084	1.371
45208	203.150	70.7643	192.0310	185.1527	0.815	0.786	-3.582	-0.687
45239	273.150	66.5585	379.2297	381.2440	1.126	1.132	0.558	0.944
45206	143.150	59.7508	55.4670	54.9402	0.282	0.279	-0.950	-0.153
45240	273.150	55.9400	514.2637	531.6101	1.283	1.327	3.373	0.806
45218	203.150	50.9290	332.8987	341.0574	1.017	1.042	2.451	1.185
45217	163.150	47.9533	197.9780	191.5433	0.709	0.686	-3.250	-2.079
45228	203.150	44.4948	512.1458	494.6270	1.367	1.320	-3.421	-6.367
45216	143.150	43.0376	141.3929	146.3927	0.518	0.536	3.536	3.765
45227	163.150	42.4258	316.3296	296.6938	1.002	0.940	-6.207	-6.376
45226	143.150	37.5326	309.9597	327.7556	0.990	1.047	5.741	4.921

90 NO.OF DATA POINTS : 14. AVG.DEV.% : 2.792 2.478

Region III

APPENDIX II.1c

ARGON-NITROGEN

20.10% Ar - 79.90% N_2

42) Crain-Sonntag-Van Wylen data (26)

(*) The Benedict-Webb-Rubin equation with the constants in Table VI and the combining rule listed in Table V.

Region IIa

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
42146	143.150	267.4465	32.0607	32.0357	0.730	0.729	-0.078	-0.023
42136	143.150	309.2727	28.9924	28.9810	0.761	0.761	-0.039	0.020
42137	163.150	355.3577	31.7417	31.7002	0.843	0.841	-0.131	0.183
42126	143.150	427.5476	22.5736	22.5588	0.822	0.821	-0.065	0.010
42116	143.150	492.8127	20.0981	20.0907	0.843	0.843	-0.037	0.043
42127	163.150	473.7466	24.8134	24.7885	0.878	0.877	-0.100	0.172
42128	203.150	478.2187	32.4482	32.3922	0.931	0.929	-0.173	-0.048
42117	163.150	567.7827	21.1445	21.1239	0.897	0.896	-0.097	0.149
42118	203.150	552.8657	28.3217	28.2736	0.939	0.938	-0.170	-0.053
42106	143.150	683.2188	15.2075	15.2006	0.884	0.884	-0.045	0.038
42096	143.150	787.5466	13.4068	13.4044	0.899	0.899	-0.018	0.064
42107	163.150	757.1248	16.2863	16.2737	0.921	0.920	-0.077	0.130
42108	203.150	762.3215	20.8770	20.8485	0.955	0.953	-0.136	-0.037
42139	273.150	723.3748	30.5344	30.5271	0.985	0.985	-0.024	-0.480
42097	163.150	906.9717	13.7771	13.7695	0.933	0.933	-0.055	0.129
42098	203.150	981.2927	18.1690	18.1447	0.961	0.959	-0.134	-0.042
42129	273.150	960.9087	23.0554	23.0531	0.988	0.988	-0.010	-0.362
42086	143.150	1091.4797	9.9573	9.9644	0.925	0.926	0.071	0.145
42076	143.150	1258.2595	8.7275	8.7325	0.935	0.935	0.057	0.126
42087	163.150	1209.7795	10.5063	10.5020	0.949	0.949	-0.041	0.110
42088	203.150	1215.0596	13.3205	13.3064	0.971	0.970	-0.106	-0.031
42119	273.150	1151.6196	19.2751	19.2687	0.990	0.990	-0.033	-0.330
42077	163.150	1448.5393	8.8485	8.8462	0.957	0.957	-0.026	0.106
42078	203.150	1404.6489	11.5674	11.5566	0.975	0.974	-0.094	-0.025
42109	273.150	1529.7983	14.5397	14.5384	0.992	0.992	-0.009	-0.234
42066	143.150	1743.4185	6.4180	6.4208	0.953	0.953	0.044	0.102
42056	143.150	2010.0095	5.6025	5.6049	0.959	0.959	0.044	0.098
42067	163.150	1932.8196	6.7030	6.7024	0.968	0.968	-0.009	0.097
42068	203.150	1936.5183	8.4478	8.4426	0.981	0.981	-0.061	-0.005
42099	273.150	1833.3784	12.1500	12.1456	0.994	0.993	-0.036	-0.224

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
42057	163.150	2313.2288	5.6303	5.6304	0.973	0.973	0.001	0.094
42058	203.150	2238.6387	7.3272	7.3221	0.984	0.983	-0.070	-0.019
42089	273.150	2435.5088	9.1575	9.1570	0.995	0.995	-0.005	-0.145
42046	143.150	2794.4497	4.0908	4.0934	0.970	0.970	0.063	0.109
42047	163.150	3087.6995	4.2457	4.2472	0.979	0.980	0.013	0.088
42048	203.150	3086.2593	5.3382	5.3355	0.988	0.988	-0.051	-0.009
42079	273.150	2918.7285	7.6491	7.6471	0.996	0.996	-0.026	-0.141
42036	143.150	3210.5686	3.5620	3.5643	0.974	0.974	0.066	0.108
42038	203.150	3567.6890	4.6251	4.6231	0.990	0.989	-0.044	-0.005
42037	163.150	3693.8389	3.5612	3.5623	0.983	0.983	0.031	0.097
42069	273.150	3877.3884	5.7629	5.7622	0.997	0.997	-0.011	-0.095
42026	143.150	4446.7344	2.5893	2.5923	0.980	0.981	0.114	0.150
42059	273.150	4645.5547	4.8116	4.8109	0.997	0.997	-0.015	-0.082
42027	163.150	4932.3750	2.6787	2.6794	0.987	0.987	0.025	0.079
42028	203.150	4918.4336	3.3647	3.3632	0.993	0.992	-0.045	-0.012
42016	143.150	5127.8750	2.2519	2.2536	0.983	0.984	0.074	0.108
42018	203.150	5685.6445	2.9134	2.9124	0.994	0.993	-0.035	-0.004
42017	163.150	5898.1836	2.2440	2.2454	0.989	0.989	0.061	0.109
42049	273.150	6172.8437	3.6241	3.6237	0.998	0.998	-0.010	-0.057
42039	273.150	7397.1758	3.0254	3.0250	0.998	0.998	-0.014	-0.052
42029	273.150	9827.3047	2.2783	2.2779	0.999	0.999	-0.018	-0.042
42019	273.150	11776.1953	1.9017	1.9013	0.999	0.999	-0.020	-0.038

00 NO.OF DATA POINTS : 52. AVG.DEV.% : 0.054 0.101

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
42229	273.150	94.0333	250.7660	250.2551	1.052	1.050	-0.204	0.153
42186	143.150	104.4960	52.6543	52.1810	0.468	0.464	-0.899	-0.151
42176	143.150	120.4480	49.6630	49.3154	0.509	0.506	-0.700	-0.177
42187	163.150	115.8319	73.4067	73.0958	0.635	0.632	-0.424	1.121
42188	203.150	117.9483	116.1640	115.8876	0.822	0.820	-0.238	0.883
42219	273.150	112.7039	201.3600	201.6220	1.012	1.014	0.130	-0.218
42177	163.150	139.0489	64.7137	64.5347	0.672	0.670	-0.277	0.681
42178	203.150	136.3790	101.3830	101.2931	0.829	0.829	-0.089	0.596
42209	273.150	149.6529	147.2450	147.8040	0.983	0.987	0.380	-0.616
42166	143.150	167.2139	42.6232	42.5061	0.607	0.605	-0.275	-0.105
42156	143.150	192.7440	39.4172	39.3622	0.647	0.646	-0.139	-0.040
42167	163.150	185.3069	52.7867	52.7516	0.731	0.730	-0.066	0.467
42168	203.150	188.1059	75.8412	75.8011	0.856	0.855	-0.053	0.215
42199	273.150	179.3580	121.9510	122.3397	0.976	0.979	0.319	-0.774
42157	163.150	222.2219	46.1456	46.0914	0.766	0.765	-0.117	0.307
42158	203.150	217.4899	66.6188	66.5560	0.869	0.868	-0.094	0.112
42189	273.150	228.1859	91.5235	91.7076	0.973	0.975	0.201	-0.826
42147	163.150	296.3477	36.8294	36.8035	0.815	0.815	-0.070	0.274
42148	203.150	299.9467	49.8681	49.7926	0.897	0.896	-0.151	0.002
42179	273.150	285.4707	76.4437	76.5286	0.974	0.975	0.111	-0.823
42138	203.150	346.7786	43.6388	43.6138	0.909	0.907	-0.171	-0.028
42169	273.150	379.1426	57.7358	57.7668	0.977	0.977	0.054	-0.719
42159	273.150	454.4116	48.3021	48.3071	0.979	0.979	0.010	-0.663
42149	273.150	603.5627	36.5033	36.5048	0.983	0.983	0.004	-0.529

CO NO.OF DATA POINTS : 24. AVG.DEV.% : 0.216 0.437

Region IIb

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
42197	163.150	86.9488	91.3696	90.3507	0.593	0.587	-1.115	1.981
42198	203.150	85.5348	162.7900	161.2667	0.835	0.827	-0.936	1.614
42196	143.150	75.2537	61.6761	61.1143	0.395	0.392	-0.911	0.854
42207	163.150	72.4145	109.3820	108.1956	0.592	0.585	-1.085	2.821
42208	203.150	73.9957	195.9480	194.3231	0.870	0.863	-0.829	1.823
42239	273.150	70.8141	375.4355	376.9688	1.186	1.191	0.408	0.477
42206	143.150	65.3056	69.8336	69.1705	0.388	0.385	-0.949	1.555
42240	273.150	59.0825	518.0237	533.3318	1.365	1.406	2.955	0.252
42217	163.150	54.4535	178.5740	178.3123	0.726	0.725	-0.147	1.414
42218	203.150	53.7315	350.0505	357.5115	1.128	1.152	2.131	0.583
42216	143.150	47.1374	156.8620	156.1883	0.629	0.627	-0.429	-0.520
42227	163.150	45.4221	311.1526	312.7808	1.056	1.061	0.523	-0.137
42228	203.150	46.5231	517.0906	530.1433	1.443	1.479	2.524	-0.799
42226	143.150	41.0306	310.7546	305.3052	1.085	1.066	-1.754	-1.576

90 NO.OF DATA POINTS : 14. AVG.DEV.% : 1.193 1.172

APPENDIX II.2

ARGON-NEON

46.82% Ar - 53.18% Ne

55) data obtained in this research

(*) The Benedict-Webb-Rubin equation with the constants in Table VI and the combining rule listed in Table V.

NO.	T-K	V-CC/MOLE	PEXP-ATM.	PCAL-ATM.	Z	ZCAL	DEV.%	DEV.% (*)
55531	114.991	363.2747	23.0201	23.1058	0.886	0.890	0.372	-1.840
55532	119.955	363.4907	24.3612	24.3476	0.900	0.899	-0.056	-1.776
55533	124.971	363.6836	25.6365	25.5976	0.909	0.908	-0.152	-1.484
55534	129.960	363.8047	26.8951	26.8406	0.917	0.916	-0.202	-1.229
55535	134.911	364.0417	28.1403	28.0624	0.925	0.923	-0.277	-1.064
55536	139.894	364.2256	29.3887	29.2923	0.932	0.929	-0.328	-0.926
55537	144.862	364.4265	30.6215	30.5143	0.939	0.935	-0.350	-0.801
55516	140.109	84.3535	111.1405	108.1167	0.815	0.793	-2.721	-4.675
55517	144.897	84.4031	118.0617	115.0789	0.838	0.817	-2.526	-4.003
55524	129.946	141.0499	61.9733	61.4046	0.820	0.812	-0.918	-3.563
55525	134.817	141.1069	65.6966	65.0602	0.838	0.830	-0.969	-3.031
55526	139.706	141.2140	69.4062	68.6943	0.855	0.846	-1.026	-2.637
55527	144.888	141.2959	73.2814	72.5449	0.871	0.862	-1.005	-2.254

13 NO.OF DATA POINTS : 13. AVG.DEV.% : 0.839 2.253

APPENDIX II.c

NEON-NITROGEN

51.40% Ne - 48.60% N_2

65) data obtained in this research

(*) The Benedict-Webb-Rubin equation with the constants in Table VI and the combining rule listed in Table V.

NO.	T=K	V=CC/MOLE	PEXP=ATM.	PCAL=ATM.	Z	ZCAL	DEV.%	DEV.% (*)
65433	100.007	402.6147	17.7377	17.9601	0.870	0.881	1.254	-0.588
65434	110.004	402.9885	20.0688	20.2413	0.896	0.904	0.860	-0.238
65435	119.996	403.3867	22.3561	22.4963	0.916	0.922	0.627	-0.046
65436	130.005	403.8376	24.6201	24.7373	0.932	0.936	0.476	0.029
65437	140.000	404.2776	26.8629	26.9652	0.945	0.949	0.381	0.034
65415	119.993	115.2259	66.6378	67.4189	0.780	0.789	1.172	-1.122
65416	129.999	115.3740	76.7380	77.5116	0.830	0.838	1.008	-0.562
65417	139.998	115.5250	86.6882	87.5243	0.872	0.880	0.965	-0.293
65424	109.999	211.5929	34.9077	35.4123	0.818	0.830	1.446	-0.731
65425	119.999	211.8280	39.7452	40.1460	0.855	0.864	1.008	-0.343
65426	129.999	212.0789	44.4903	44.8316	0.884	0.891	0.767	-0.153
65427	139.994	212.3250	49.1737	49.4860	0.909	0.915	0.635	-0.090

12 NO.OF DATA POINTS : 12. AVG.DEV.% : 0.883 0.352

ALL DATA HAVE BEEN PROCESSED

STOP 0
EXECUTION TERMINATED

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