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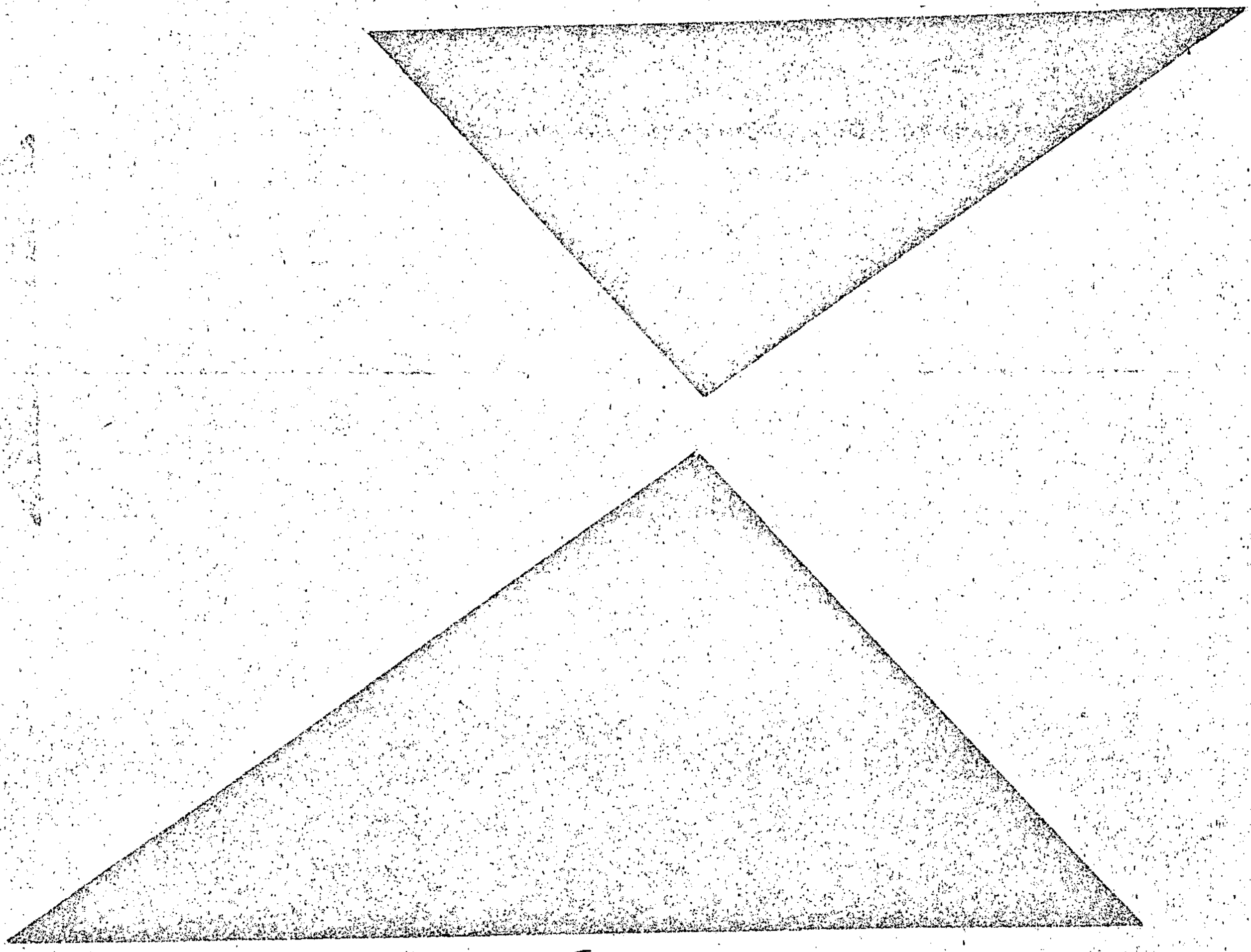

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AN EQUATION OF STATE FOR OXYGEN AND NITROGEN

II

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ABSTRACT

Preliminary equations of state for oxygen and nitrogen are presented which are the result of least squares fitting of the available P-ρ-T data, heat capacities at constant volume, and data to establish the criteria for phase equilibrium, simultaneously. The equation for nitrogen is applicable to 10,000 atmospheres at temperatures from 70 K to 1300 K, and the equation for oxygen to 350 atmospheres for temperatures from 56 K to 323 K. The development of the functional form of the equation of state, data weighting methods and the techniques employed for least squares fitting of related data are discussed. Comparisons of the equation of state developed with selected values of experimental P-ρ-T data, and heat capacity values are included for both fluids. Topics to be investigated in the continuing studies of these equations of state for this project are summarized.

TABLE OF CONTENTS

I. INTRODUCTION

The accomplishments for the period, October 1 to December 31, 1971, are summarized below. Detailed discussions of each item are included in this report.

1. The study of the P-ρ-T data for nitrogen published by various experimenters has been completed. This study was to determine the relative agreement of measurements made in the same or adjacent ranges of temperature and pressure by different experimenters, and to determine more appropriate relative weights for the data in the least squares fit to an equation of state.
2. The study of the functional form of the equation of state has resulted in the development of an optimized 32 term equation of state, which may be used for both oxygen and nitrogen, with the appropriate coefficients. This equation of state was determined using the method of least squares with a systematic procedure for optimization of the form of the equation.
3. The development of procedures for including values of P-ρ-T, C_v, and the criteria for phase equilibrium in a weighted least squares fit for calculating the coefficients of the equation of state was completed.
4. Alternate methods of weighting of the data for the least squares fit of the equation of state were investigated.
5. Values of the constant volume heat capacity, C_v, were predicted for nitrogen using the principle of corresponding states. The method was tested by comparing measured

values of C_v for fluorine with values predicted by this procedure. The C_v values for nitrogen were subsequently used in the determination of the equation of state for nitrogen by the method noted in 3 above.

6. New equations of state for oxygen and nitrogen have been determined using the results of the studies summarized above.
7. Comparisons of the new equations of state have been made with the data used in their determination. Selected comparisons are given in this report to illustrate the accuracy of the equations.

The new equations of state for oxygen and nitrogen presented in this report must be regarded as preliminary. The section, "Continuing Studies", notes several additional tests of the equations which have not been completed. In particular, it will be necessary to reconcile any differences between the critical points of the equations, and values of the critical properties determined by measurement.

II. DEVELOPMENT OF THE EQUATION OF STATE

A. Selection of Oxygen P-ρ-T Data

The literature reporting measurements of P-ρ-T values for oxygen is summarized in Table I. An evaluation of the data from references [0-1] through [0-21] and preliminary values from the measurements later published in [0-22] is included in reference [1]. The data of Weber [0-22] are a self-consistent set of measurements which cover most of the range of the data summarized in Table I. Because of their high precision and consistency, the data of [0-14], [0-15], and [0-22] were selected for use in the determination of the equation of state for oxygen.

Table I

SUMMARY OF P-ρ-T DATA FOR OXYGEN

	Source	Temperature Range (K)	Pressure Range (atm)	Number of Data Points
	Amagat [0-1]	273 - 473	1 - 3000	83
†	Baly and Donnan [0-2]	69 - 89	-	18
	Baxter and Starkweather [0-3]	273	0.4 - 1	4
†	Biltz, Fischer, and Wunnenberg [0-4]	78	-	2
†	Drugman and Ramsay [0-5]	-	1	2
†	Germann [0-6]	100 - 136	2 - 23	15
	Holborn and Otto [0-7]	273 - 373	24 - 100	27
†	Inglis and Coates [0-8]	74, 79	0.13, 0.26	2
	Kamerlingh Onnes and Hyndman [0-9]	273 - 293	22 - 66	31
	Kamerlingh Onnes and Kuypers [0-10]	156 - 233	20 - 61	75
†	Kanda [0-11]	59 - 87	-	4
	Kuypers and Kamerlingh Onnes [0-12]	273 - 293	20 - 61	50
†	Mathias and Kamerlingh Onnes [0-13]	62 - 152	-	7
*	Michels, Schamp, and deGraaf [0-14]	273 - 323	22 - 134	40
*	Nijhoff and Keesom [0-15]	120 - 233	2.8 - 9.3	43
**	Timrot and Borisoglebskii [0-16]	83 - 153	9 - 193	283
†	Timrot and Borisoglebskii [0-17]	79 - 153	0.2 - 47	10
†	Van Itterbeek and Van Dael [0-18]	66 - 90	-	7
**	Van Itterbeek and Verbeke [0-19]	64 - 90	2 - 149	68
**	Van Itterbeek and Verbeke [0-20]	77, 90	98 - 874	15
	Van Urk and Nijhoff [0-21]	273 - 293	34 - 62	28
*	Weber [0-22]	54 - 300	1 - 330	1503
†	Weber [0-23]	150 - 154.566	Saturated Liquid and Vapor Densities	40

* Data sets used in fit

** Liquid data only

B. Selection of Nitrogen P-ρ-T Data

The sources of experimental P-ρ-T data for nitrogen are summarized in Table II. Some of the data sets for the high pressure (1000 to 10,000 atm.) vapor region are not in agreement. A lack of concordance of the data for the liquid region was also observed. A selection of data sets to be used in the determination of the equation of state was therefore required. In some cases the basis for selection was, of necessity, subjective.

Liquid Data

The references reporting liquid data for nitrogen [N-8], [N-11], [N-13], [N-29], [N-33], [N-34], and [N-36] do not appear to be in agreement within the uncertainties of the respective data sets. The data of [N-8], [N-11], [N-13], and [N-36] were selected for use in the determination of the equation of state for nitrogen. These data sets were selected because of their mutual concordance.

High Pressure Vapor Data

The high pressure vapor P-ρ-T data of [N-23], [N-26], and [N-27] were selected for determining the equation of state. There is a mutual concordance among the data from these three references. The data of [N-20] and [N-21] are assumed to be the smoothed results of the same experimental investigation, but do not exhibit concordance among themselves. The high pressure data of [N-6], [N-31], and [N-32] are not in close agreement with the selected data from [N-23], [N-26], and [N-27], and were not included in the determination of the equation of state.

Saturated Liquid Data and Data Along Melting Line

Values of density as a function of temperature for the saturated liquid [N-12], [N-30] and for the liquid along the melting line [N-14] were not used in determining the equation of state. The use of these data will be investigated as a part of the continuing studies.

Table II

SUMMARY OF P-ρ-T DATA FOR NITROGEN

Source	Temperature Range (K)	Pressure Range (atm)	Number of Data Points
* Amagat [N-1]	273 - 473	1 - 3000	149
* Bartlett [N-2]	273	1 - 1000	9
* Bartlett et al. [N-3]	273 - 673	1 - 1000	52
* Bartlett et al. [N-4]	203 - 293	100 - 1000	42
* Benedict [N-5]	90 - 273	99 - 1500	25
* Benedict [N-6]	98 - 473	981 - 5879	124
Canfield [N-7]	133 - 273	2 - 300	152
** Cockett et al. [N-8]	85 - 120	50 - 200	63
Crain et al. [N-9]	143 - 273	2 - 500	90
Friedman [N-10]	80 - 300	1 - 200	201
** Gibbons [N-11]	72 - 77	22 - 124	17
* † Goldman, Scrase and Cockett [N-12]	78 - 125	1 - 32	80
** Golubev and Dobrovolskii [N-13]	78 - 133	49 - 484	59
*†† Grilly and Mills [N-14]	64 - 120	75 - 3441	10
* Hall [N-15]	103 , 113	2 - 9	8
* Heuse and Otto [N-16]	273	0.04 - 0.1	8
Holborn and Otto [N-17]	273 - 673	24 - 100	66
* Holborn and Otto [N-18]	273 - 403	20 - 100	24
* Kamerlingh Onnes and van Urk [N-19]	124 - 293	30 - 50	143
* Malbrunot and Vodar [N-20]	473 - 1273	1000 - 4000	63
* Malbrunot [N-21]	473 - 1273	800 - 5000	191
Michels et al. [N-22]	273 - 423	20 - 80	56
Michels et al. [N-23]	273 - 423	200 - 3000	147
* Miller, Stroud, and Brandt [N-24]	21	9 - 260	10
Otto, Michels and Wouters [N-25]	298 - 423	45 - 400	63
Robertson and Babb [N-26]	308 - 673	1600 - 10,000	170
Saurel [N-27]	423 - 1073	10 - 900	87
* Smith and Taylor [N-28]	273 - 473	34 - 319	40
* ** Streett and Staveley [N-29]	77.35 - 120.23	4.32 - 680.46	107
* † Terry et al. [N-30]	77 - 104	1 - 10	15
* Tsiklis and Polyakov [N-31]	294 - 673	1600 - 10,000	69
* Tsiklis [N-32]	323 - 423	3000 - 6000	21
* ** Van Itterbeek and Verbeke [N-33,N-34]	65 - 90	15 - 840	80
* Verschoyle [N-35]	273 - 293	25 - 205	36
** Weber [N-36]	80 - 140	30 - 266	76

* Data sets not used in fit
** Liquid data
† Saturated liquid data
†† Liquid on freezing line

C. The Determination of the Equation of State

Although a satisfactory equation of 35 terms had been developed [4], no systematic procedure had been employed to ascertain that the best 35 terms were used or that 35 was an optimum number of terms. A procedure for such a study using the method of least squares had been developed in a separate project in the Mechanical Engineering Department at the University of Idaho [5]. This procedure was employed in this study and is described below.

Stepwise Multiple Regression Analysis

To systematize the choice of terms to be used in the equation of state for nitrogen, the computer program developed by G. L. Rose [5] was utilized to analyze the following comprehensive equation of state.

$$
\begin{aligned}
P = \rho RT &+ \rho^2(N_1T + N_2T^{1/2} + N_3 + N_4/T + N_5/T^2 + N_6/T^3 + N_7/T^4) \\
&+ \rho^3(N_8T^2 + N_9T + N_{10} + N_{11}/T + N_{12}/T^2) \\
&+ \rho^4(N_{13}T^2 + N_{14}T + N_{15} + N_{16}/T + N_{17}/T^2) \\
&+ \rho^5(N_{18}T^2 + N_{19}T + N_{20} + N_{21}/T + N_{22}/T^2) \\
&+ \rho^6(N_{23}/T + N_{24}/T^2) \\
&+ \rho^7(N_{25}/T + N_{26}/T^2) \\
&+ \rho^8(N_{27}/T + N_{28}/T^2) \\
&+ \rho^9(N_{29}/T + N_{30}/T^2) \\
&+ \rho^{11}(N_{31}/T + N_{32}/T^2) \\
&+ \rho^3(N_{33}/T^2 + N_{34}/T^3 + N_{35}/T^4)\ \exp\ (-\gamma\rho^2) \\
&+ \rho^5(N_{36}/T^2 + N_{37}/T^4)\ \exp\ (-\gamma\rho^2) \\
&+ \rho^7(N_{38}/T^2 + N_{39}/T^3)\ \exp\ (-\gamma\rho^2) \\
&+ \rho^9(N_{40}/T^2 + N_{41}/T^3 + N_{42}/T^4)\ \exp\ (-\gamma\rho^2) \\
&+ \rho^{11}(N_{43}/T^2 + N_{44}/T^3 + N_{45}/T^4)\ \exp\ (-\gamma\rho^2) \\
&+ \rho^{13}(N_{46}/T^2 + N_{47}/T^3 + N_{48}/T^4)\ \exp\ (-\gamma\rho^2) \\
&+ \rho^{15}(N_{49}/T^3 + N_{50}/T^4)\ \exp\ (-\gamma\rho^2) \qquad (1)
\end{aligned}
$$

Equation (1) includes the possible terms that previous experience had indicated might produce an equation appropriate to describe the P-ρ-T surface. The analysis of (1) was then designed to determine the relative significance of these selected 50 terms.

The technique of stepwise multiple regression was utilized to fit a selected data set for nitrogen. The first term was selected as the one which had the highest correlation coefficient for the data used. The second term was chosen from among the remaining terms to provide the highest correlation coefficient for two terms including the first term as selected above. This procedure was continued until all 50 terms with undetermined coefficients had been utilized in the final fit.

The fitting process was then repeated with 45 terms by deleting the five terms which had the lowest F-statistics of the group of 50, and repeated again with 43 terms after the deletion of two more terms with the least significant F-values. To eliminate further terms which had small or negligible contributions to the fit, the analysis of the F-statistics of the coefficients was continued by deleting one term with each successive fit. This procedure was continued until an equation was obtained with only one term with an F-statistic below the value for significance at the one percent level. This resulted in the equation (2) below, which, when fit to P-ρ-T data for the entire range of available measurements for either oxygen or nitrogen, had 31 coefficients with F-values above the level for significance.

$$\begin{aligned} P = \rho RT &+ \rho^2(N_1T + N_2T^{\frac{1}{2}} + N_3 + N_4/T + N_5/T^2) \\ &+ \rho^3(N_6T + N_7 + N_8/T + N_9/T^2) \\ &+ \rho^4(N_{10}T + N_{11} + N_{12}/T) \\ &+ \rho^5(N_{13}) \\ &+ \rho^6(N_{14}/T + N_{15}/T^2) \\ &+ \rho^7(N_{16}/T) \\ &+ \rho^8(N_{17}/T + N_{18}/T^2) \\ &+ \rho^9(N_{19}/T^2) \\ &+ \rho^3(N_{20}/T^2 + N_{21}/T^3)\ \exp\ (-\gamma\rho^2) \\ &+ \rho^5(N_{22}/T^2 + N_{23}/T^4)\ \exp\ (-\gamma\rho^2) \\ &+ \rho^7(N_{24}/T^2 + N_{25}/T^3)\ \exp\ (-\gamma\rho^2) \\ &+ \rho^9(N_{26}/T^2 + N_{27}/T^4)\ \exp\ (-\gamma\rho^2) \\ &+ \rho^{11}(N_{28}/T^2 + N_{29}/T^3)\ \exp\ (-\gamma\rho^2) \\ &+ \rho^{13}(N_{30}/T^2 + N_{31}/T^3 + N_{32}/T^4)\ \exp\ (-\gamma\rho^2) \end{aligned} \tag{2}$$

The 32 coefficient equation fit to the P-ρ-T data alone provided an acceptable representation of the P-ρ-T surface, but further refinements in the method of formulation were then made for improving the calculation of derived properties, particularly of specific heats in the liquid range and at temperatures near the critical value.

Simultaneous Fitting

To incorporate related thermodynamic data with the P-ρ-T data in a single determination of the equation of state, procedures were developed for including values of C_v, and the criteria for phase equilibrium between saturated liquid and saturated vapor points in a simultaneous least squares fitting technique. The procedures for including the conditions of phase equilibrium with the method of least squares are described in [6]. The method employed allows integration of functions for property calculation along hypothetical isotherms through the two-phase region. This is accomplished by satisfying thermodynamic relations for two-phase equilibrium of a pure substance. In the least squares formulation incorporating P-ρ-T data, heat capacity data, and these equilibrium conditions, the sums of squares of the weighted residuals of the following functions are minimized simultaneously.

1. $P = \Sigma N_i P_i(\rho,T) + \rho RT$ (3)
2. $C_v = \Sigma N_i C_i(\rho,T) + C_v^o$ (4)
3. $\Sigma N_i P_i(\rho_{SL}, T_S) - \Sigma N_i P_i(\rho_{SV}, T_S) = (\rho_{SV} - \rho_{SL})RT_S$ (5)
4. $\Sigma N_i G_i = P_S(\frac{1}{\rho_{SL} - \rho_{SV}}) + RT \ln(\frac{\rho_{SL}}{\rho_{SV}})$ (6)

where: P, ρ, T, and C_v are respectively the pressure, density, temperature, and constant volume heat capacity of data points used in the fit, P_S, T_S, ρ_{SL}, ρ_{SV}, are the saturation pressure, saturation temperature, density of the saturated liquid, and density of the saturated vapor respectively.

the P_i are the individual terms of the equation of state,

the $C_i(\rho,T)$ are the terms of the integral representation

$$C_i(\rho,T) = \int_0^\rho \frac{T}{\rho^2} \left[\frac{\partial^2 P_i(\rho,T)}{\partial T^2}\right] d\rho, \tag{7}$$

the G_i are the terms of the integral representation used to calculate the difference in Gibbs function across the two phase region given by

$$G_i = \int_{\rho_{SL}}^{\rho_{SV}} \left[\frac{P_i(\rho,T_S)}{\rho^2} - \frac{RT_S}{\rho}\right] d\rho, \tag{8}$$

and the N_i are the coefficients of the equation of state to be determined.

The equation for C_v for oxygen from Goodwin and Weber [O-24] was used to calculate values for the determination of the oxygen equation of state. This equation was also used with the principle of corresponding states to calculate values of C_v for nitrogen. (See Appendix A.) The nitrogen and oxygen C_v data were used in the simultaneous fitting primarily to give an equation which exhibits proper behavior of the first and second derivatives.

Saturated liquid and saturated vapor densities were required in the formulation of the phase equilibrium criteria. These were calculated for nitrogen from the simultaneous solution of the vapor pressure equation and the interim equation of state both from [4] on intervals of 0.25 degree K between the triple point and the critical point. The values for oxygen were calculated on two degree intervals between the triple point and the critical point by the simultaneous solution of the vapor pressure equation from [7] and two equations of state determined by separate fits to the liquid and vapor regions alone.

The coefficients for equation (2) determined by a simultaneous weighted least squares fit using a procedure suggested by McCarty [8], for oxygen and nitrogen are given in Tables III and IV respectively.

Weighting of Data for Oxygen and Nitrogen

Preliminary weighting of the P-ρ-T data for the least squares determination of the equation of state was based on the estimated uncertainties in density for each data set. Details of the weighting function are given in [2]. The weights used for the P-ρ-T data were reviewed and changed several times during the development of the equation of state. In addition, data sets found to be in disagreement with one another were reviewed, and the data considered less accurate were removed from the compiled values used for establishing the equation.

After the development of an interim functional form of the equation of state [4] for both oxygen and nitrogen, which provided an acceptable fit to the entire range of P-ρ-T data, the behavior of the equation was further examined by calculating derived thermodynamic properties (i.e., enthalphy, entropy, and the heat capacities, C_p and C_v). The equation of state was found to exhibit thermodynamically consistent characteristics over much of the range of pressure and temperature for which P-ρ-T data were available. However, values of heat capacity for both fluids calculated using this equation exhibit erratic behavior in the liquid region and near the critical temperature, indicating the need for further modification.

Weights for the further development of the form of the equation of state were determined using the root mean squared (rms) deviations in pressure along isotherms and isochores from separate fits of the interim equation reported in [4] to selected data in the liquid and vapor regions. Rms deviations were calculated along isotherms or isochores of data of each author from

$$\text{rms} = \frac{[\Sigma(P_{calc} - P_{data})/P_{data}]^{\frac{1}{2}}}{N}, \qquad (9)$$

where P_{calc} is the pressure calculated from the appropriate liquid or vapor equation of state, P_{data} is the experimental pressure, and N is the number of data points on the isotherm or isochore. The weight applied to each data point was calculated from

$$WT = \frac{1}{(\text{rms} \times P_{data})^2} \qquad (10)$$

Following the development of the functional form of (2) the equation of state using P-ρ-T data, constant volume specific heat data and data to describe the criteria for liquid-vapor equilibrium were added to the compiled P-ρ-T values used for determining the form of the equation, and new coefficients for (2) determined by a simultaneous least squares fit of these related data as discussed in the preceding section.

The weights applied to the C_v data and to the saturation data used in fitting phase equilibrium criteria were arbitrary, and were specified to make the effects of each of the data points compatible with P-ρ-T points in the same region of temperature and pressure. The coefficients for equation (2) given in Tables III and IV were determined by simultaneous least squares fits of P-ρ-T data weighted using equation (10), to calculated C_v data weighted by the relation, $WT = 10{,}000/(C_v)^2$, and to phase equilibrium criteria defined by saturation data weighted with the equation, $WT = 100/(P + 0.01)$, for both oxygen and nitrogen.

Table III

Coefficients for the Equation of State (2) for Oxygen*

$N_1 = -0.170887398436657 \times 10^{-2}$
$N_2 = 0.233008642369091$
$N_3 = -0.433993811662375 \times 10^{1}$
$N_4 = 0.177172970652312 \times 10^{3}$

$N_5 = -0.120035790297848 \times 10^{5}$
$N_6 = 0.768602601713339 \times 10^{-4}$
$N_7 = -0.838050060230444 \times 10^{-2}$
$N_8 = -0.112945718198605 \times 10^{2}$

$N_9 = 0.249933236222486 \times 10^{4}$
$N_{10} = -0.392210483256747 \times 10^{-5}$
$N_{11} = 0.412792194660784 \times 10^{-2}$
$N_{12} = 0.385058781582990 \times 10^{-2}$

$N_{13} = -0.286274514156647 \times 10^{-4}$
$N_{14} = -0.656972420621184 \times 10^{-4}$
$N_{15} = -0.868270744076546 \times 10^{-1}$
$N_{16} = 0.248888126044600 \times 10^{-5}$

$N_{17} = -0.480347612728966 \times 10^{-8}$
$N_{18} = 0.698141409980872 \times 10^{-4}$
$N_{19} = -0.851009706892387 \times 10^{-6}$
$N_{20} = 0.171174677742300 \times 10^{4}$

$N_{21} = -0.337130293024023 \times 10^{6}$
$N_{22} = -0.120824987128239 \times 10^{2}$
$N_{23} = 0.748250739682284 \times 10^{5}$
$N_{24} = -0.104770899761072 \times 10^{1}$

$N_{25} = 0.145048005360464 \times 10^{1}$
$N_{26} = -0.782522681423924 \times 10^{-4}$
$N_{27} = -0.325891488829226$
$N_{28} = 0.413896845058343 \times 10^{-8}$

$N_{29} = 0.879581917933464 \times 10^{-5}$
$N_{30} = -0.947485588746460 \times 10^{-10}$
$N_{31} = -0.251031994074357 \times 10^{-8}$
$N_{32} = -0.535541160709992 \times 10^{-7}$

$\gamma = 0.0056$ $\quad$ $R = 0.0820535$ liter-atm/mol-K

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*Coefficients are for temperatures in degrees Kelvin, pressures in atmospheres, and density in moles/liter.

Table IV

Coefficients for the Equation of State (2) for Nitrogen*

$N_1 = 0.168233003149947 \times 10^{-2}$
$N_2 = 0.889317969333137 \times 10^{-1}$
$N_3 = -0.215714364780882 \times 10^{1}$
$N_4 = 0.135526457726229 \times 10^{2}$

$N_5 = -0.349471319425168 \times 10^{4}$
$N_6 = 0.965094639633943 \times 10^{-4}$
$N_7 = 0.451766377473105 \times 10^{-2}$
$N_8 = -0.766321032555359 \times 10^{1}$

$N_9 = 0.140685343318952 \times 10^{5}$
$N_{10} = 0.484615565630029 \times 10^{-6}$
$N_{11} = 0.123095875709563 \times 10^{-2}$
$N_{12} = 0.328464757255879 \times 10^{-1}$

$N_{13} = 0.646704795937868 \times 10^{-4}$
$N_{14} = -0.195318445467739 \times 10^{-2}$
$N_{15} = -0.370690841443740$
$N_{16} = 0.100802101629611 \times 10^{-3}$

$N_{17} = -0.138899246677088 \times 10^{-5}$
$N_{18} = -0.413780754199977 \times 10^{-4}$
$N_{19} = 0.409183884146447 \times 10^{-5}$
$N_{20} = -0.115929675090774 \times 10^{5}$

$N_{21} = -0.165504443599748 \times 10^{6}$
$N_{22} = -0.772264925564061 \times 10^{2}$
$N_{23} = 0.608278718077975 \times 10^{5}$
$N_{24} = -0.126883928820405$

$N_{25} = -0.252133337856428 \times 10^{1}$
$N_{26} = -0.398579722705448 \times 10^{-3}$
$N_{27} = -0.255841840198957$
$N_{28} = -0.305544612086806 \times 10^{-7}$

$N_{29} = 0.101816557337586 \times 10^{-4}$
$N_{30} = -0.576945363745317 \times 10^{-9}$
$N_{31} = -0.621979979245604 \times 10^{-8}$
$N_{32} = 0.180237161232168 \times 10^{-7}$

$\gamma = 0.0056$ R = 0.0820535 liter-atm/mol-K

*Coefficients are for temperatures in degrees Kelvin, pressures in atmospheres, and density in moles/liter.

III. COMPARISONS OF THE EQUATION OF STATE TO P-ρ-T MEASUREMENTS

A. The Equation of State for Oxygen.

Figures 1 through 35 illustrate the deviations between measurements of density and density values calculated by the equation of state (2) with the coefficients from table III. The density deviation is given by $[(\rho_{exp} - \rho_{calc})/\rho_{exp}] \times 100$, where ρ_{exp} is the observed density reported by each experimenter, and ρ_{calc} the density calculated from equation (2) for each experimental pressure and temperature. The temperatures for which these comparisons are illustrated were selected to present a representative analysis of the data used in the least squares fit in determining the coefficients in Table III. Only the data used in the fit of equation (2) are included in the comparisons illustrated here (i.e., the data from [0-14], [0-15], and [0-22]). An evaluation of the P-ρ-T data from references [0-1 to [0-21] and preliminary values from the measurements later published in [0-22] is included in [1].

In addition to the data illustrated in figures 1 to 35, the density deviations for some data points exceeded the scale used in these figures. The data with density deviations in excess of ± 0.2 per cent are listed in Table V.

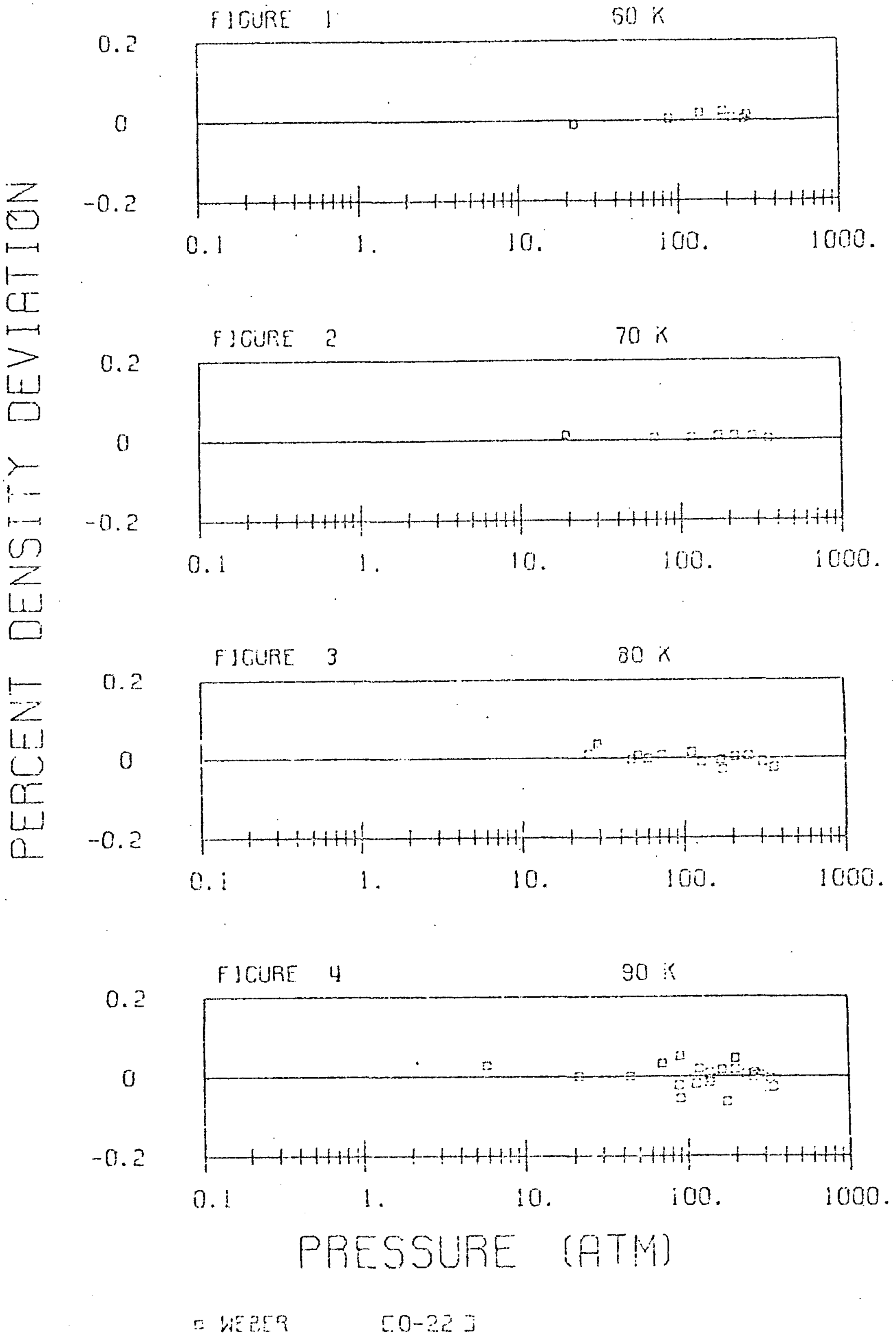
A total of 1586 P-ρ-T values were included in the least squares fit for the oxygen equation, and 1503 of these data points were from [0-22]. Figures 21 through 23 compare the data by Michels, et. al. [0-14] and values from Weber [0-22]. (The data of Weber are at 270 and 300 K, and those of Michels at 273 K, 298 K and 323 K). Figures 24 through 35 compare values by Nijhoff and Keesom [0-15] for low pressure vapor from 120 K to 233 K. Low pressure vapor values from [0-22] are illustrated in figures 5 through 9 for temperatures from 100 K to 140 K.

Systematic deviations between the data from [0-22] and equation (2) are clearly illustrated in figures 13 through 16 for temperatures from 180 K to 220 K, and may also be present at higher and lower temperatures.

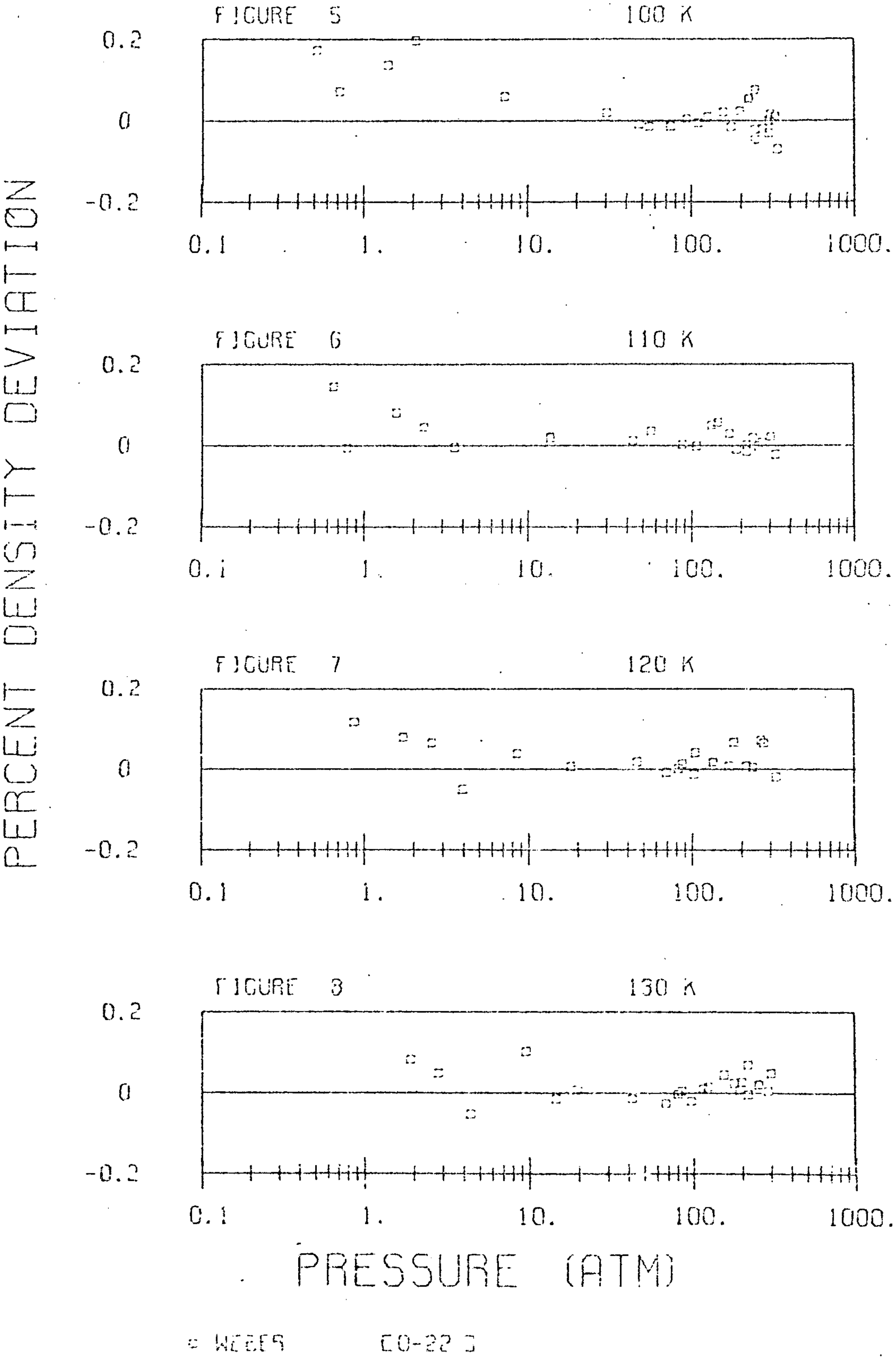
Table V

P-ρ-T DATA FOR OXYGEN WITH DENSITY DEVIATIONS IN EXCESS OF ± 0.2 PERCENT
(See Figures 1 through 27)

Temperature (K) (Figure Number)	Pressure (atm)	Percent Density Deviation	Reference
100 (Fig.5)	0.595	0.29	[0-22]
150 (Fig.10)	41.207	0.53	[0-22]
150	33.586	0.39	[0-22]
160 (Fig.11)	64.143	0.42	[0-22]
160	62.554	0.51	[0-22]
160	61.300	0.37	[0-22]
160	59.216	-0.31	[0-22]
160	58.834	-0.40	[0-22]
160	58.000	- .34	[0-22]



DEVIATIONS IN DENSITY OF EQUATION OF STATE (2) FROM EXPERIMENTAL DATA



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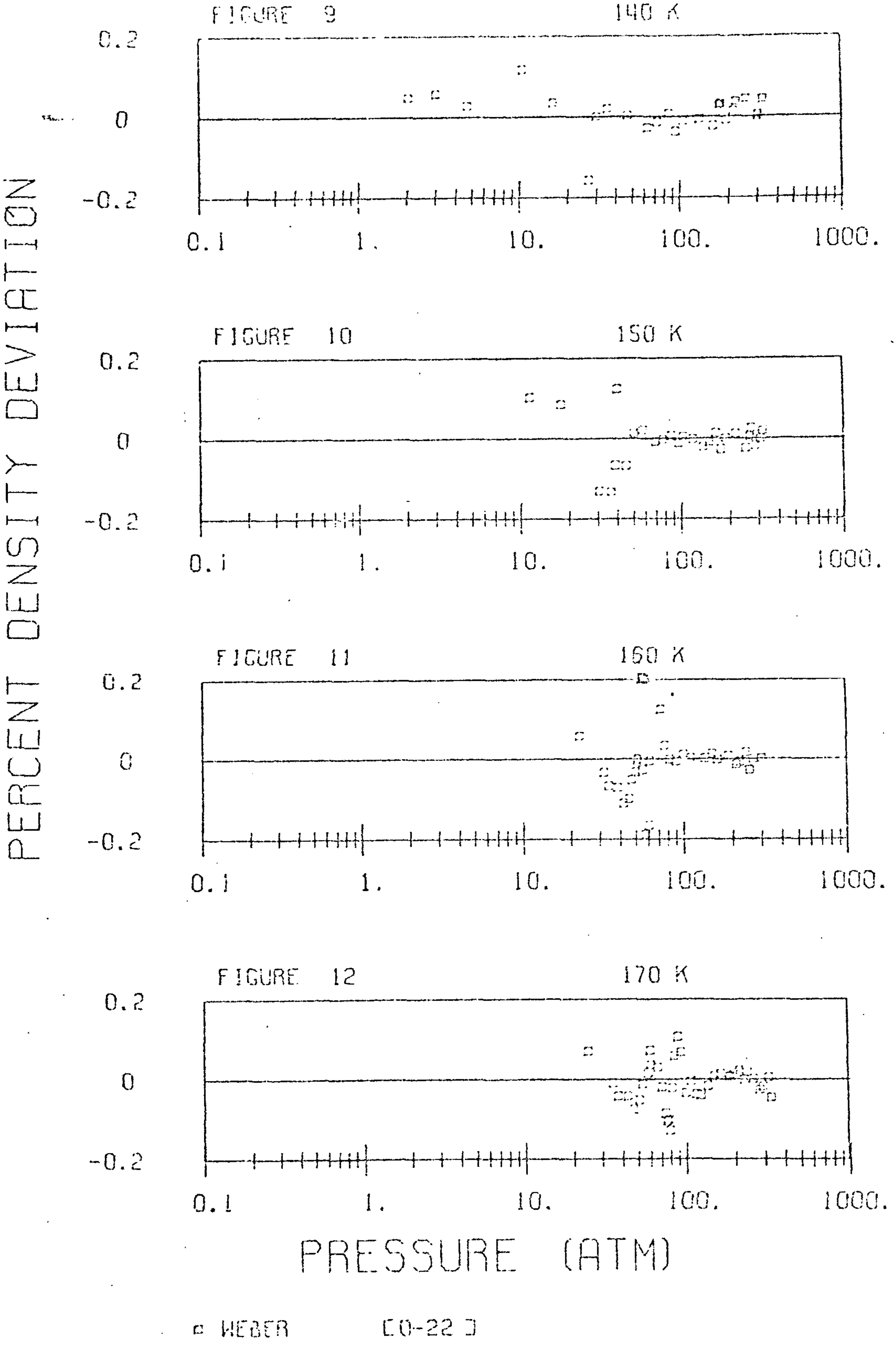

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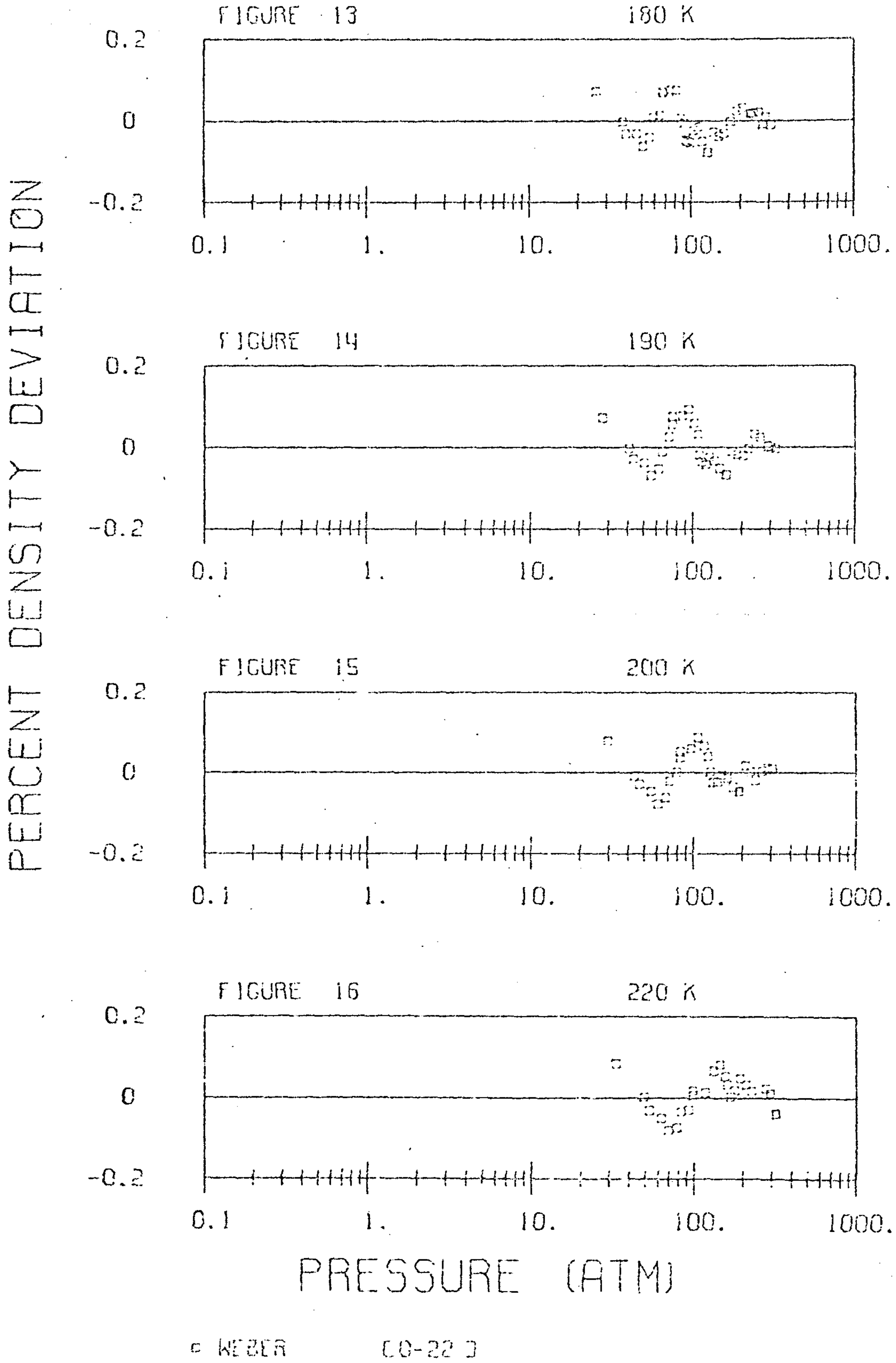

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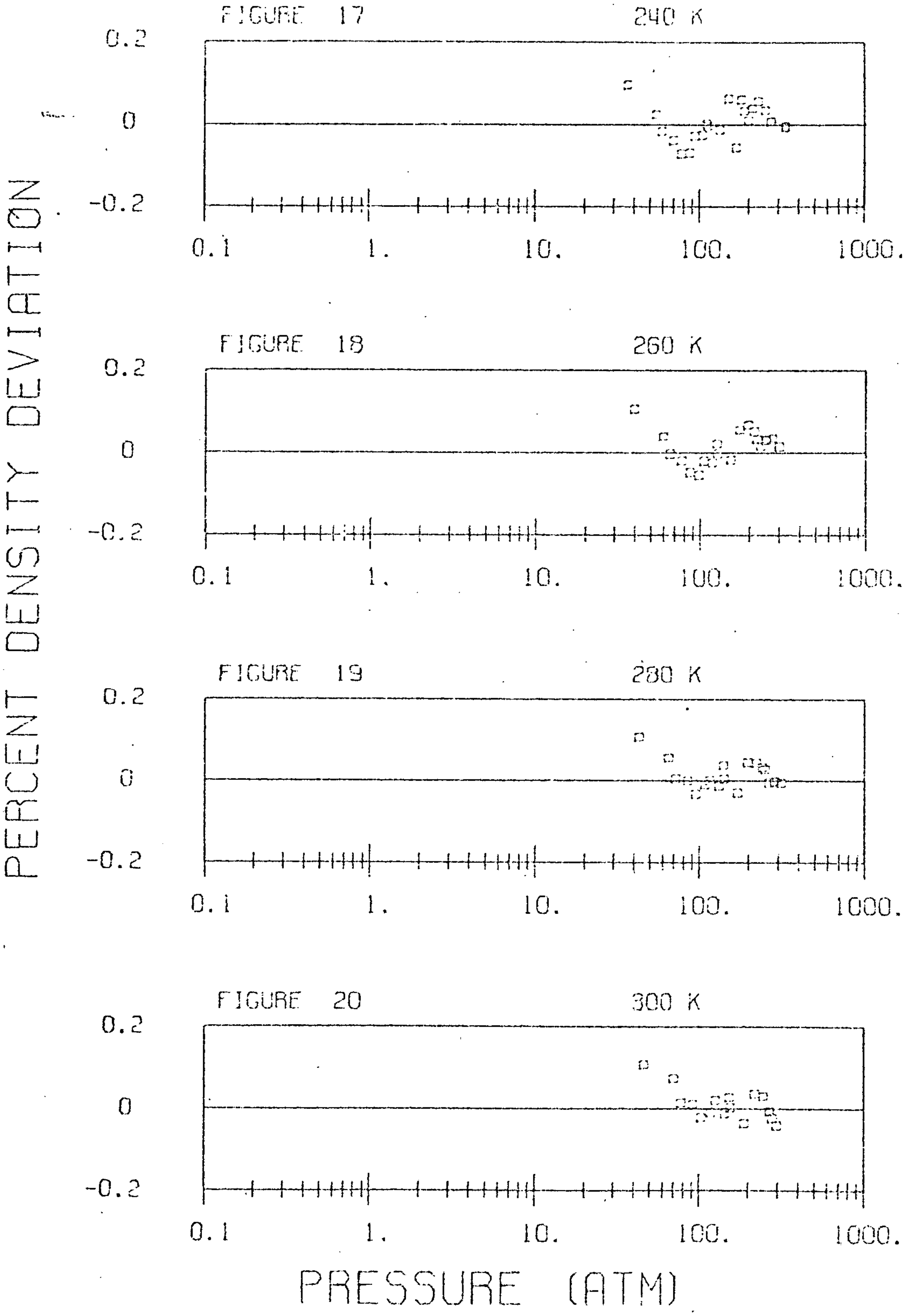
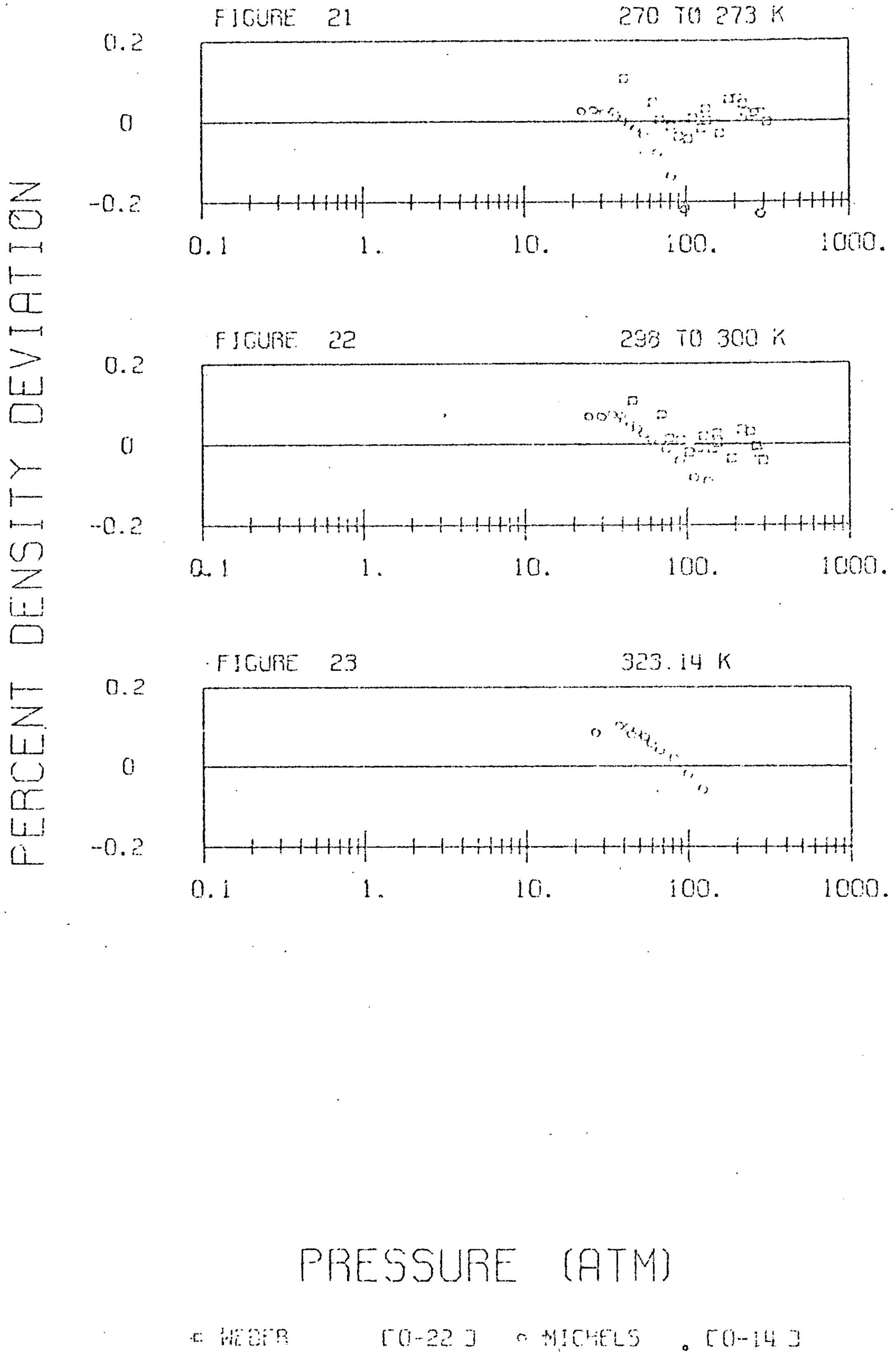


□ WEBER . [0-22]

DEVIATIONS IN DENSITY OF EQUATION OF STATE (2) FROM EXPERIMENTAL DATA



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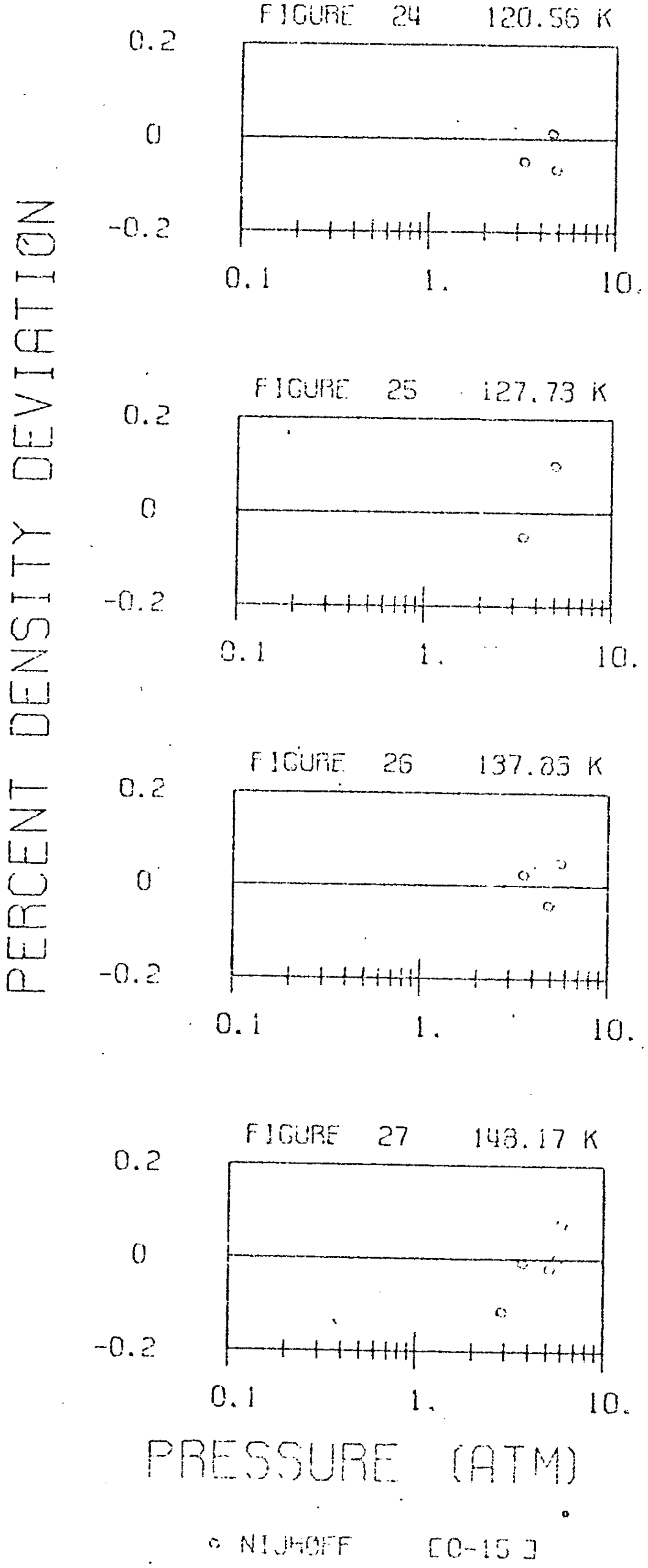
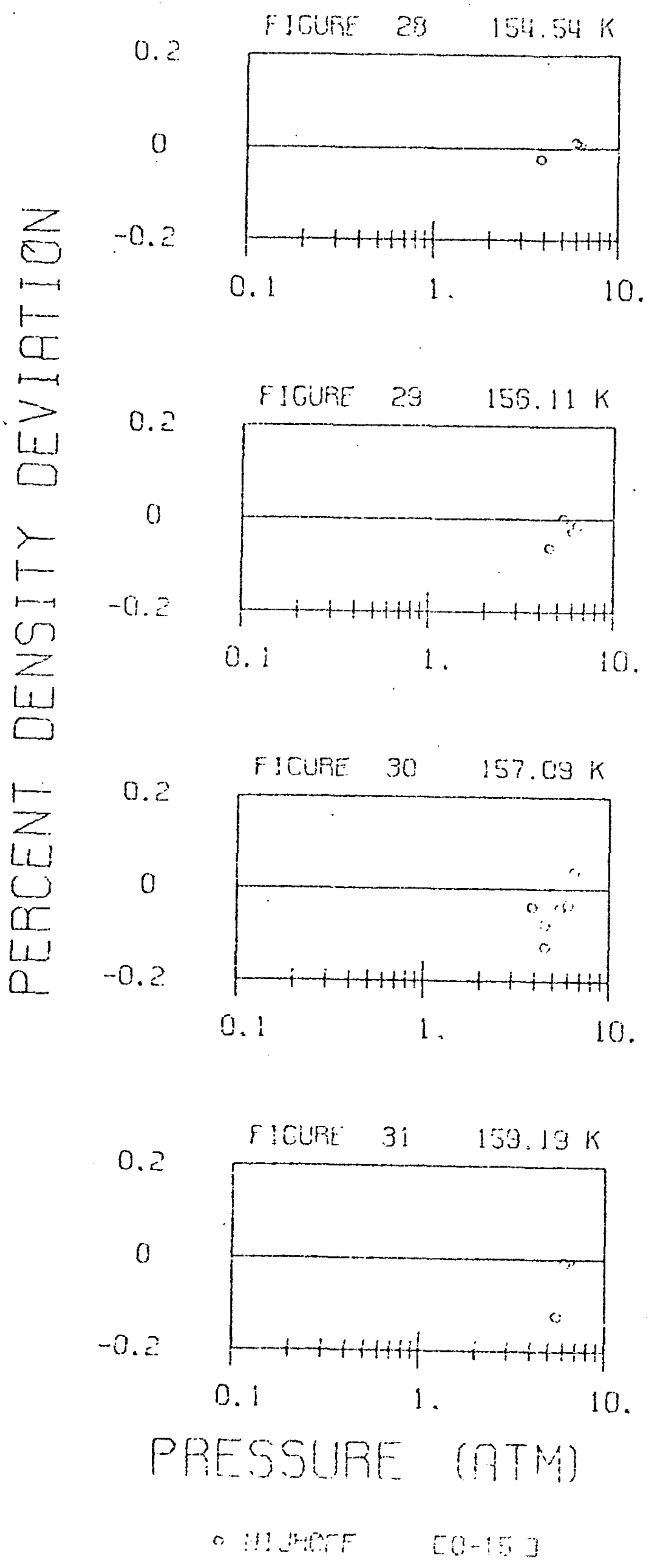
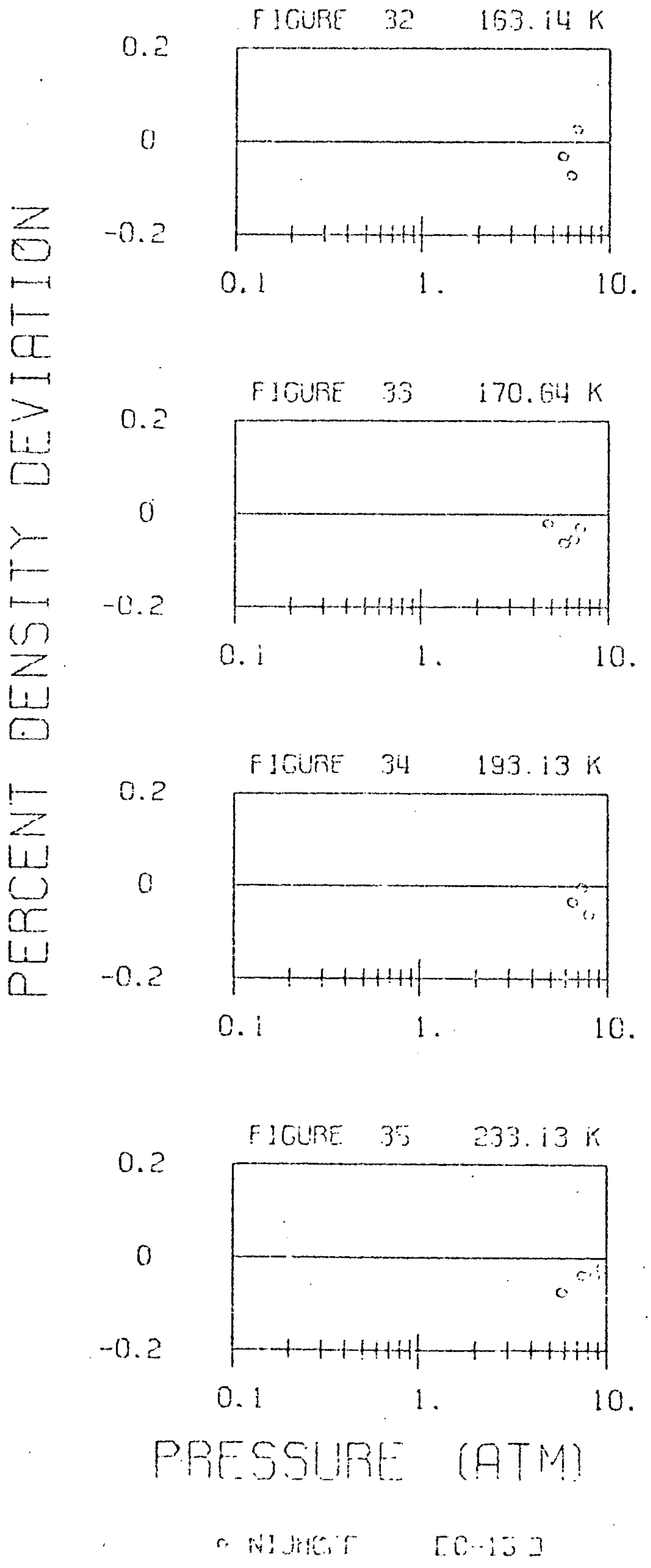


DEVIATIONS IN DENSITY OF EQUATION OF STATE (2)
FROM EXPERIMENTAL DATA



DEVIATIONS IN DENSITY OF EQUATION OF STATE (2) FROM EXPERIMENTAL DATA



DEVIATIONS IN DENSITY OF EQUATION OF STATE (2)
FROM EXPERIMENTAL DATA

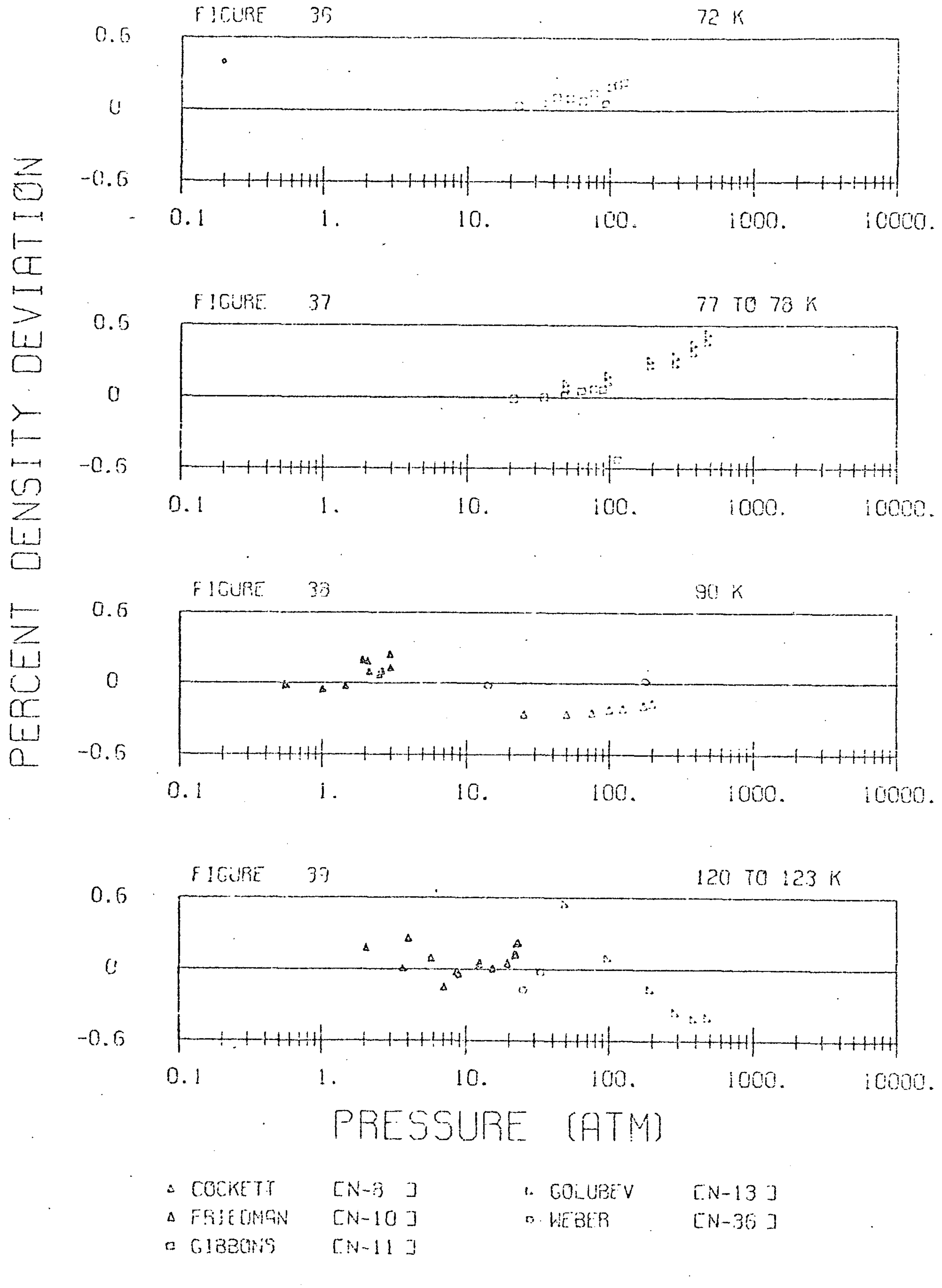
B. The Equation of State for Nitrogen

Figures 36 through 55 illustrate the deviations between measurements of density and density values calculated by the equation of state (2) with the coefficients from Table IV. The density deviation is given by $[(\rho_{exp} - \rho_{calc})/\rho_{exp})] \times 100$, where ρ_{exp} is the observed density reported by each experimenter, and ρ_{calc} the density calculated from equation (2) for each experimental pressure and temperature. The temperatures for which these comparisons are illustrated were selected to present a representative analysis of the data used in the least squares fit in determining the coefficients in Table IV. Only the data used in the fit of equation (2) are included in the comparisons illustrated here (i.e., the data from [N-7], [N-8], [N-9], [N-10], [N-11], [N-13], [N-17], [N-22], [N-23], [N-25], [N-26], [N-27], and [N-36]). An evaluation of the P-ρ-T data of [N-1] through [N-36] is included in [4].

In addition to the data shown in figures 36 through 55, the density deviations for some data points exceeded the scale used in these figures. The data with density deviations in excess of ± 0.6 percent are listed in Table VI.

A total of 1247 P-ρ-T values were included in the weighted least squares fit for the nitrogen equation. Figures 36 and 37 illustrate the liquid data of Gibbons [N-11], and Figure 37 shows the extent of agreement with the data of Golubev [N-13] at temperatures between 77 and 78 K. The vapor data of Friedman [N-10] are compared with data of Weber [N-36], Crain [N-9], Canfield [N-7], Michels [N-22], Holborn and Otto [N-17], and Otto [N-25], in Figures 39, 40, 44, and 46 for temperatures in the range of 120 K to 273 K. The high pressure data of Robertson and Babb [N-26], and Saurel [N-27] are compared in Figures 49 through 51 for temperatures in the range between 473 K and 673 K. The data of Saurel [N-27] are the only data shown on the high temperature isotherms from 773 K to 1073 K.

Discrepancies between the data sets of [N-8], [N-11], [N-13], and [N-36] illustrated in Figures 37, 38, and 39 indicate the need for further high precision measurements in the liquid range for nitrogen. The deviations indicated in [4] for the high pressure data of [N-20] and [N-21] from that of [N-26] persist in this work, although comparisons of the data of [N-20] and [N-21] are not included here.



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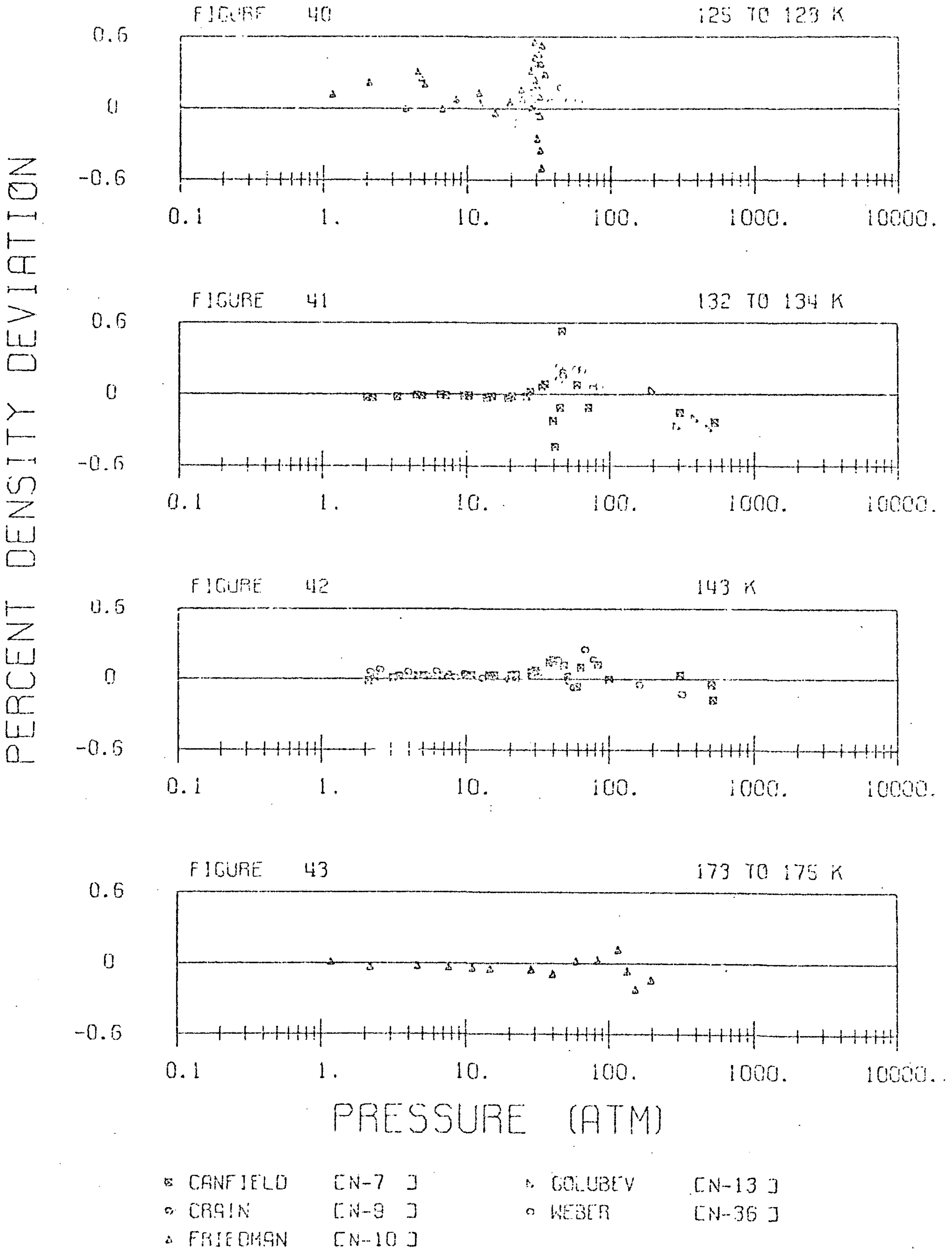

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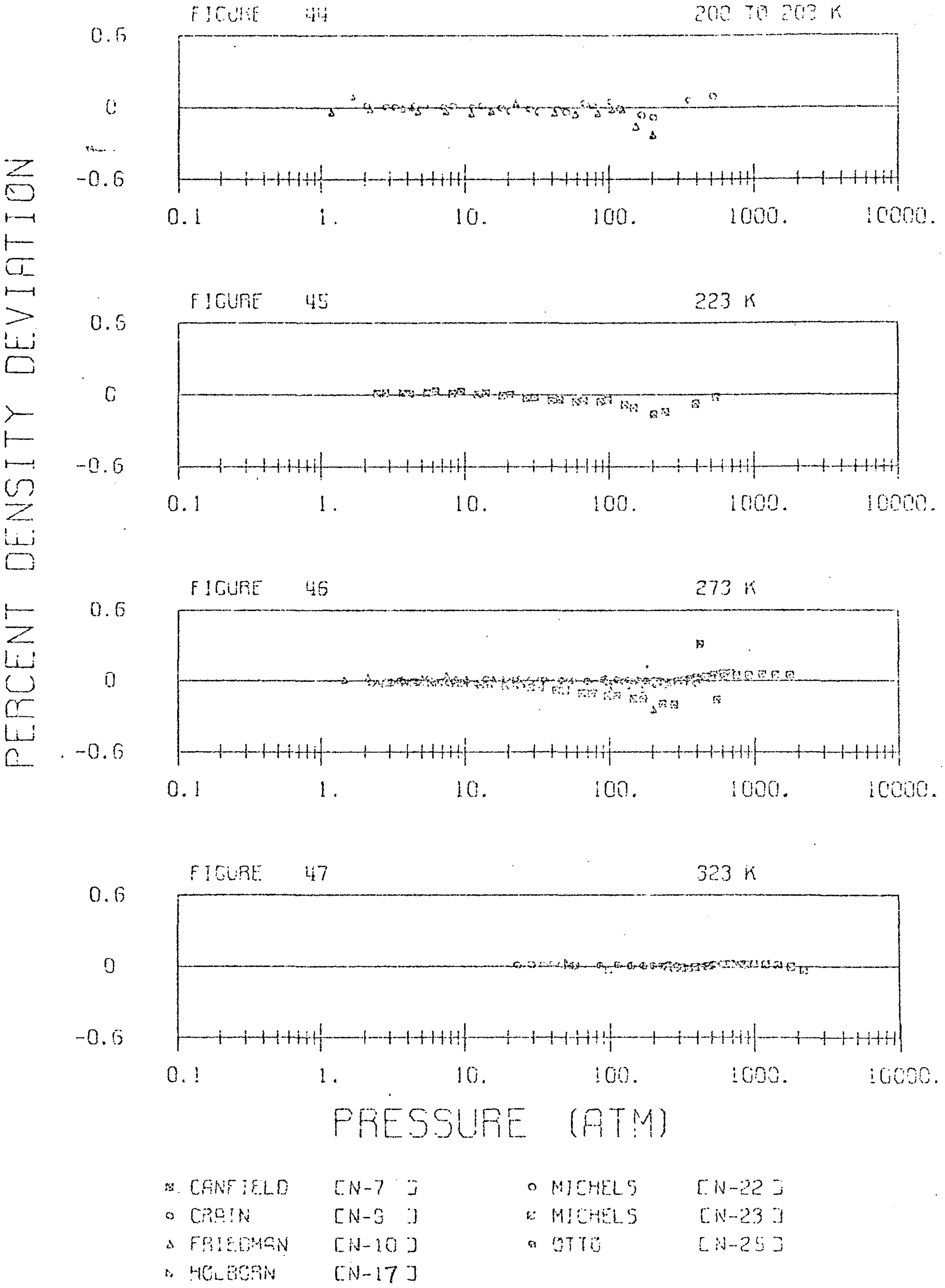

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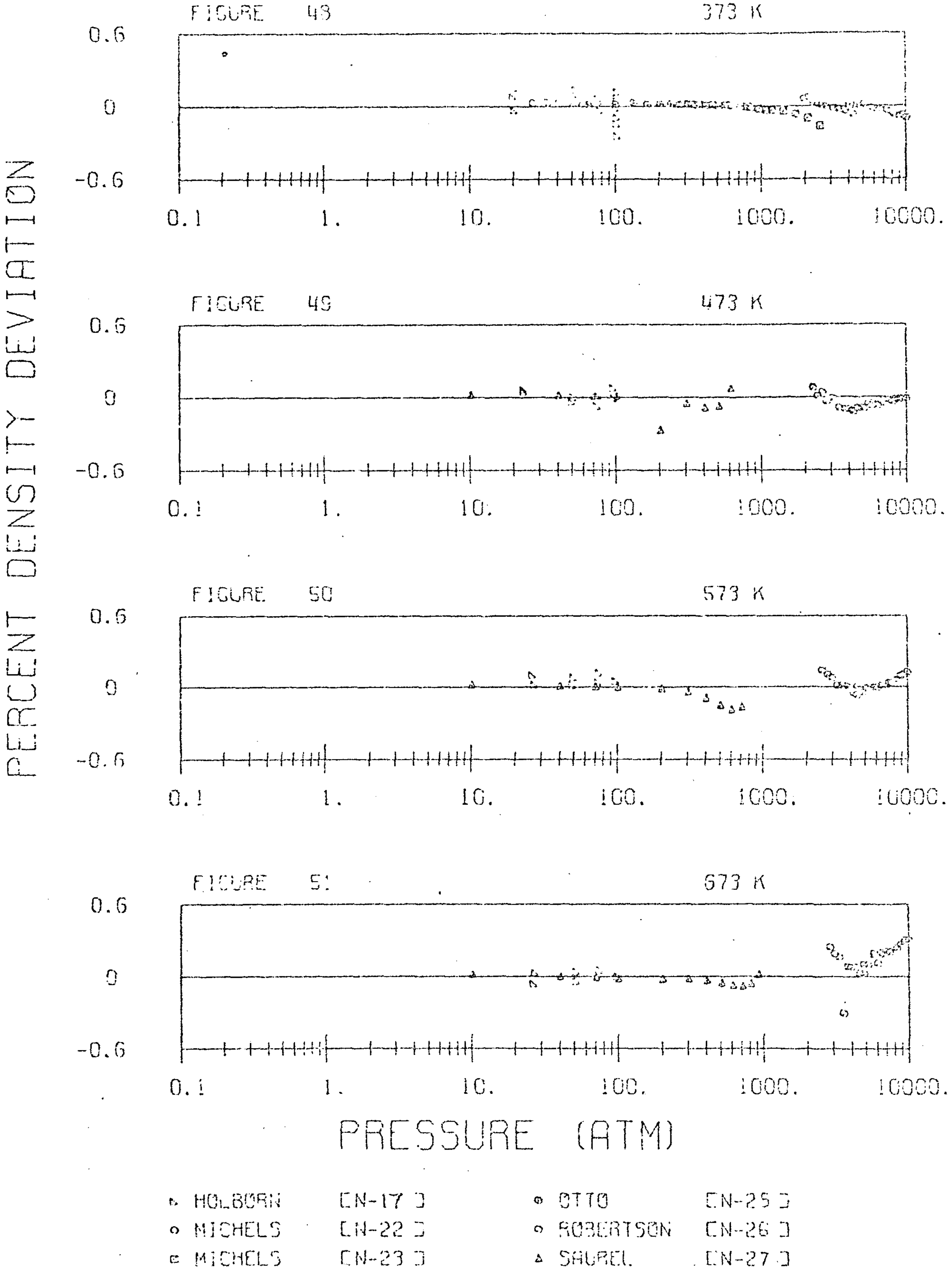

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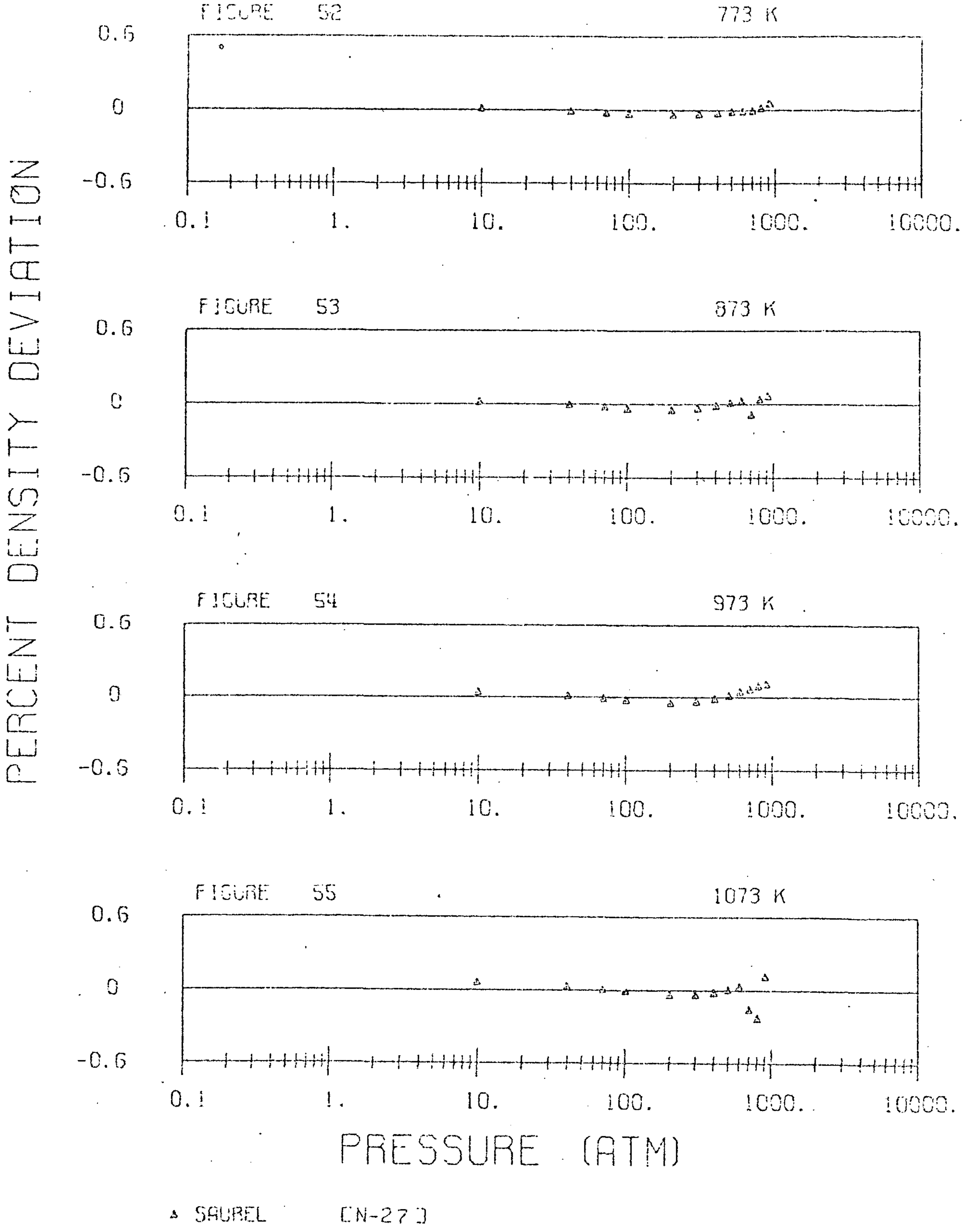


DEVIATIONS IN DENSITY OF EQUATION OF STATE (2) FROM EXPERIMENTAL DATA

Table VI

P-ρ-T DATA FOR NITROGEN WITH DENSITY DEVIATIONS IN EXCESS OF ± 0.6 PERCENT
(See Figures 36 through 55)

Temperature (K) (Figure number)	Pressure (atm)	Percent Density Deviation	Reference
120.014 (Fig.39)	4.84	-51.23	[N-10]
125.212 (Fig.40)	26.942	0.68	[N-10]
125.212	31.180	1.91	[N-10]
125.669	27.079	0.68	[N-10]
125.669	28.872	0.75	[N-10]
125.669	31.485	1.87	[N-10]
125.669	31.988	1.08	[N-10]
125.732	31.209	-1.13	[N-10]
125.732	32.766	-2.98	[N-10]
126.014	31.756	1.15	[N-10]
126.014	32.251	1.02	[N-10]
126.014	32.909	1.59	[N-10]
126.096	32.884	1.34	[N-10]
126.096	33.055	2.41	[N-10]
126.170	31.335	0.72	[N-10]
126.170	31.872	0.94	[N-10]
126.170	33.076	1.00	[N-10]
126.170	33.167	1.06	[N-10]
126.170	33.464	2.90	[N-10]
126.170	33.514	-17.19	[N-10]
126.170	34.531	0.62	[N-10]
128.000	36.030	-2.31	[N-10]
128.000	36.513	-0.69	[N-10]
128.000	36.519	-0.79	[N-10]
133.137 (Fig.41)	97.800	0.66	[N-13]
132.000	41.437	-0.98	[N-36]
134.000	44.162	-0.71	[N-36]

IV. HEAT CAPACITY VALUES CALCULATED USING THE EQUATION OF STATE (2)

A. Heat Capacities from the Equation of State for Oxygen

Heat capacities at constant pressure, C_p, and constant volume heat capacities, C_v, calculated by integration along isotherms through the two-phase region from equation (2) with coefficients from Table III for oxygen are illustrated in figures 56 and 57, respectively. Calculated values of heat capacities are shown for isobars of 1, 10, 50, 100, and 300 atmospheres. Figure 57 indicates an erratic behavior in the calculated values of C_v below a temperature of 65 K.

Figures 58 through 61 illustrate deviations of C_v values calculated from using equation (4) of Goodwin and Weber [O-24]. (Values are given for isochores of 5, 10, 13, 15, 20, 25, 30, 35, and 40 moles per liter, covering the range of applicability of equation (4) from [O-24]). These deviations are systematic but do not exceed 4 percent except at temperatures near the critical temperature. Values which exceeded the maximum deviations shown in the figures are given in Table VII.

B. Heat Capacities from the Equation of State for Nitrogen.

Values of C_p and C_v for nitrogen calculated by integration along isotherms through the two-phase region using equation (2) with coefficients from Table IV are illustrated in figures 62 and 63, respectively. Calculated heat capacities are included in these figures for isobars of 1, 10, 50, 100, and 300 atmospheres. Erratic behavior in the calculated values of C_v below 75 K is apparent in Figure 63.

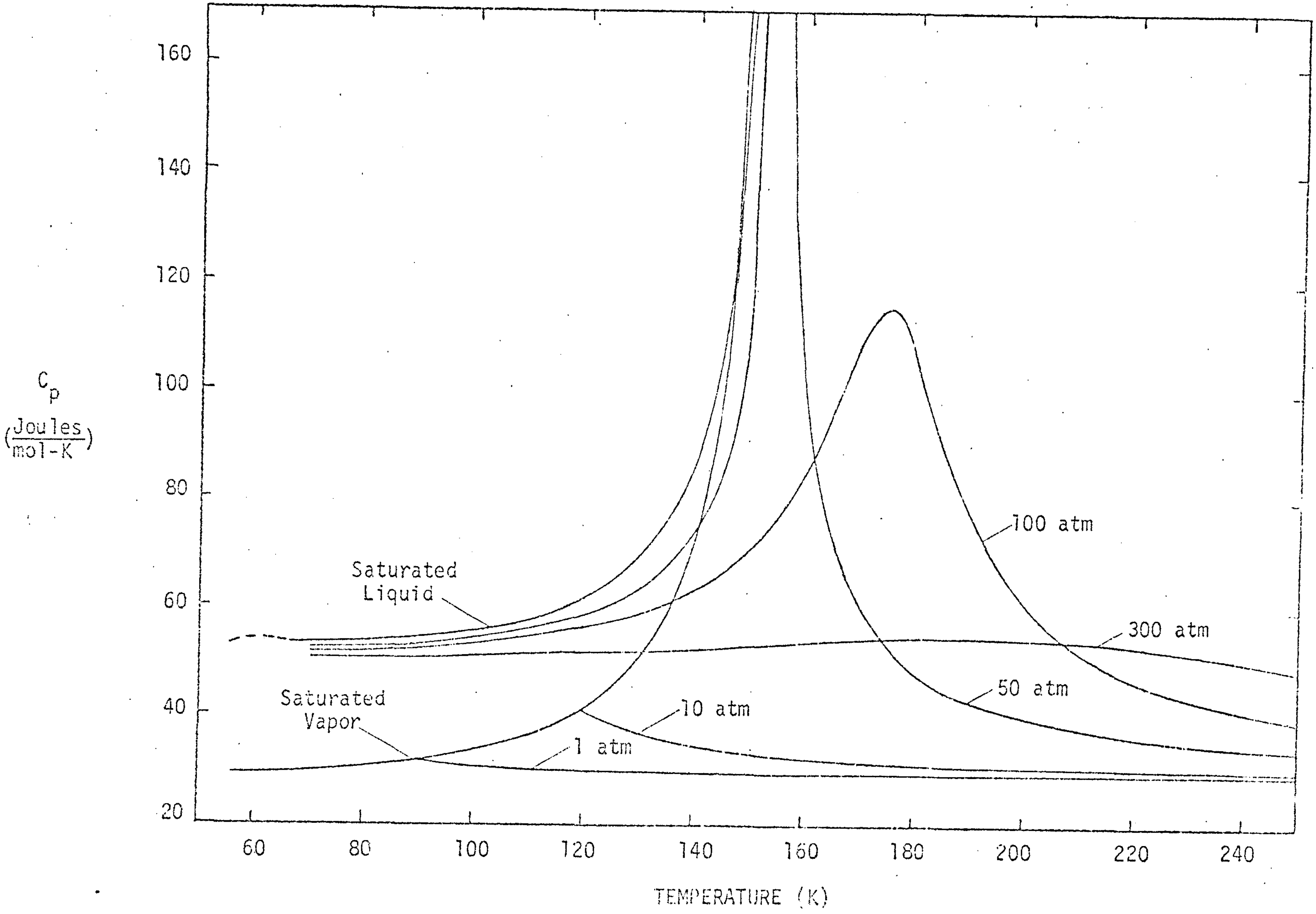


Figure 56 Constant Pressure Heat Capacity (C_p) of Oxygen Calculated with Equation of State (2) with Coefficients of Table III

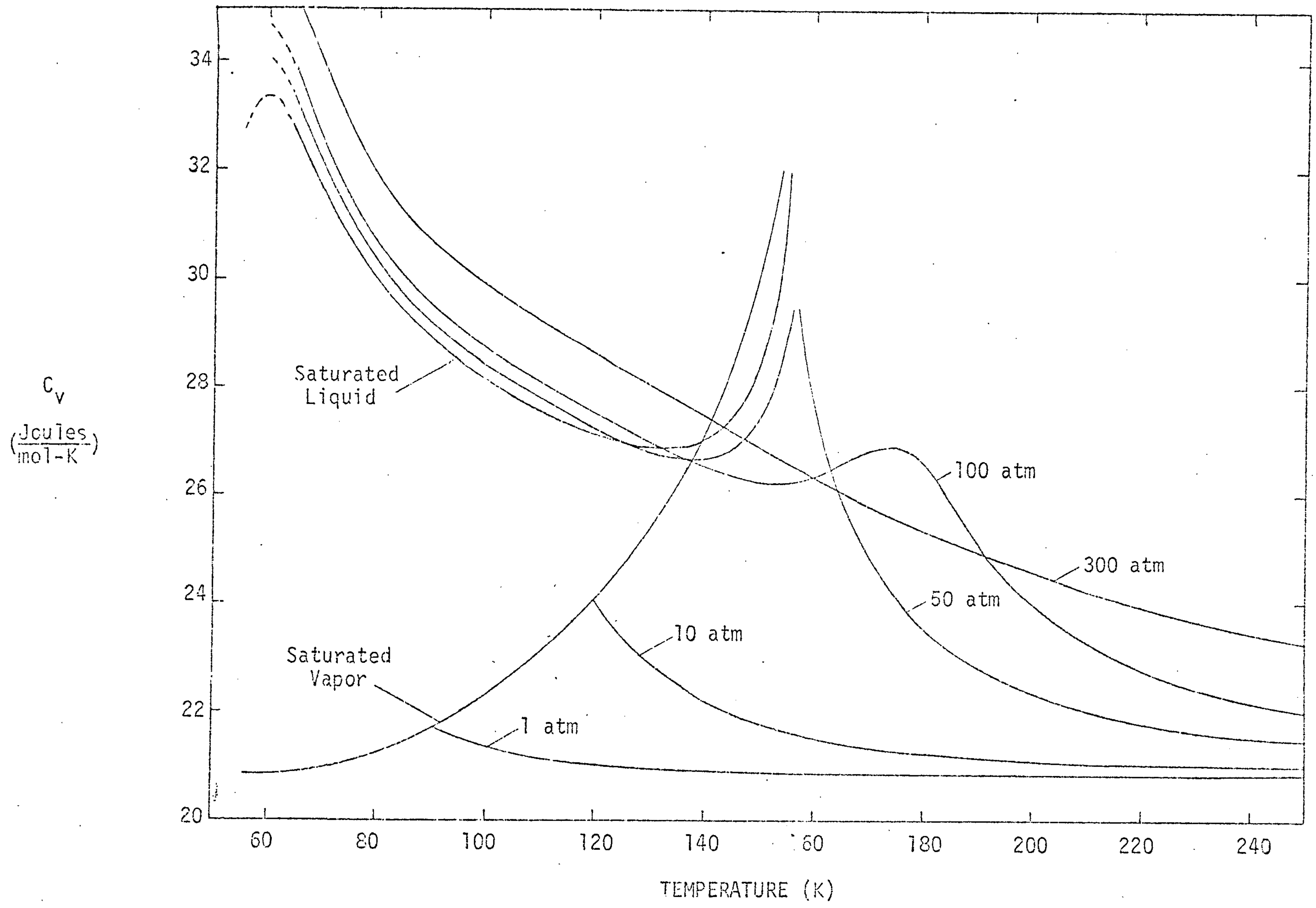
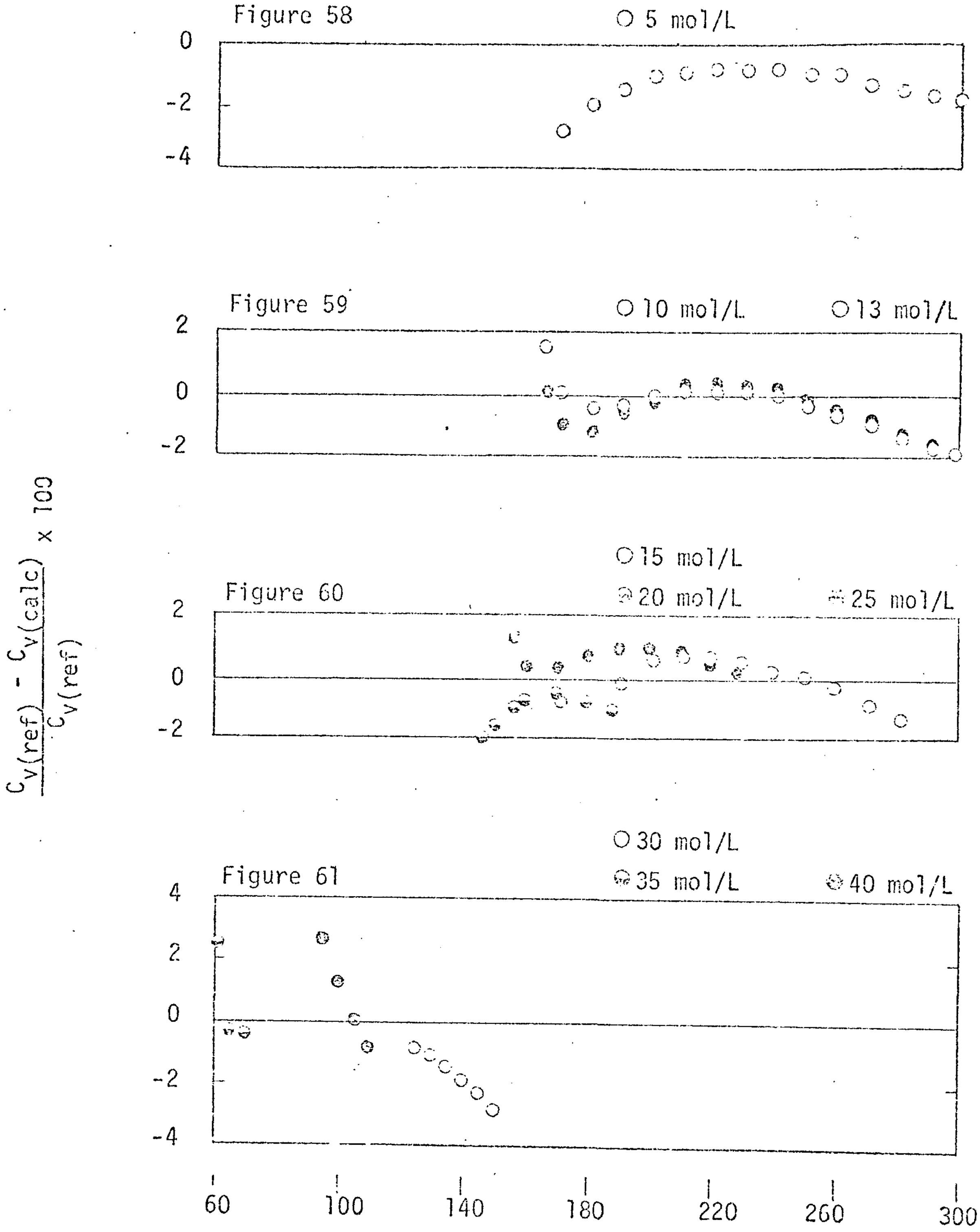


Figure 57 Constant Volume Heat Capacity (C_v) of Oxygen Calculated with Equation (2) with Coefficients of Table III



Deviations of Constant Volume Heat Capacity, C_v, of Oxygen Calculated with Equation (2) from Equation (4) of [O-24].

Table VII

Constant Volume Heat Capacity Deviations Calculated with Equation (2) from Equation (4) of [0-24] not Shown in Figures 58 to 61

ρ(mol/L) (Figure Number)	Temperature (K)	$\frac{C_{v(ref)} - C_{v(calc)}}{C_{v(ref)}} \times 100$
5 (Fig. 58)	146	-6.4
	151	-5.5
	156	-4.8
10 (Fig. 59)	156	16.4
	161	4.95
13 (Fig. 59)	156	21.0
	161	3.9
15 (Fig. 60)	156	18.6

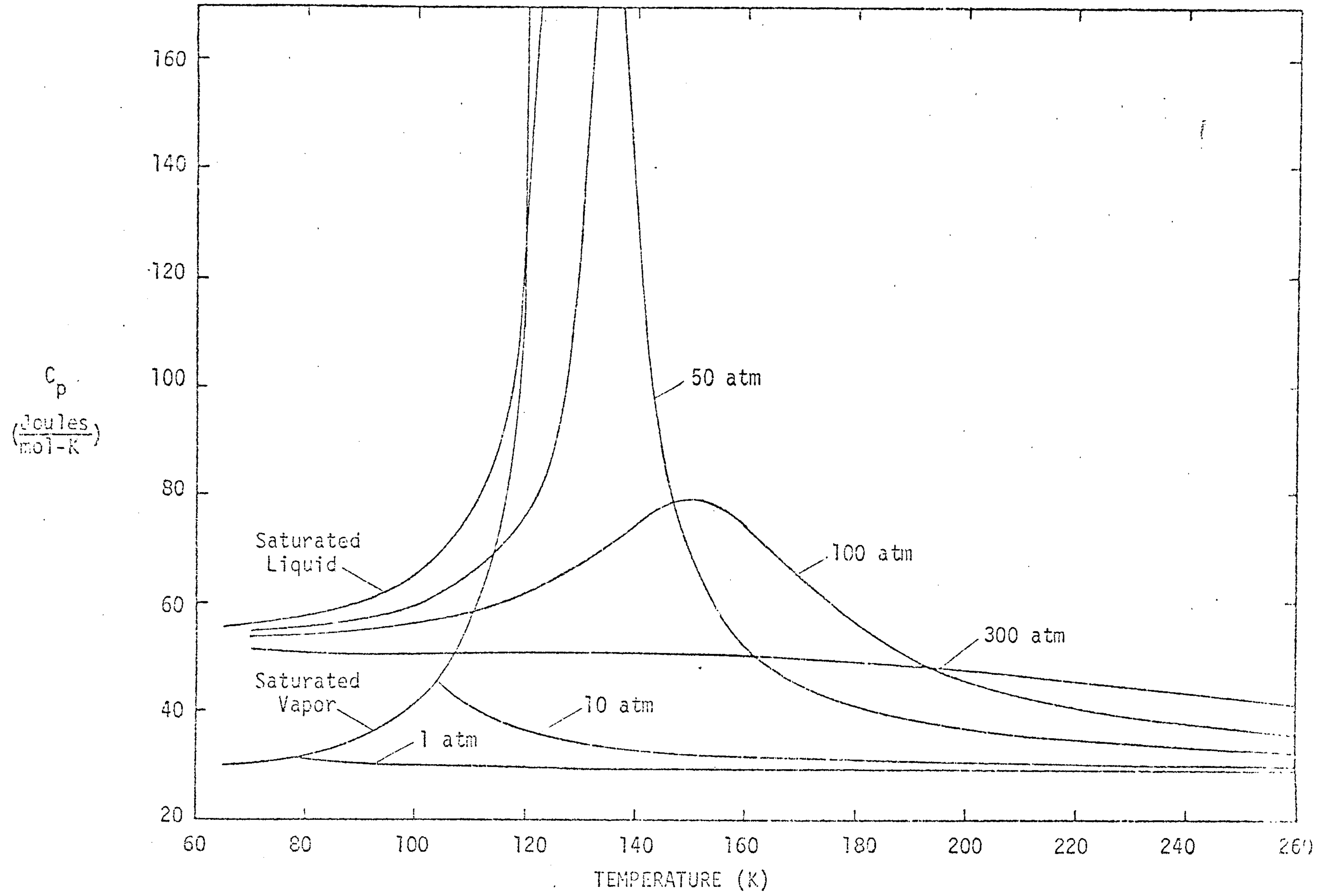


Figure 62 Constant Pressure Heat Capacity (C_p) of Nitrogen Calculated with Equation of State (2) with Coefficients of Table IV.

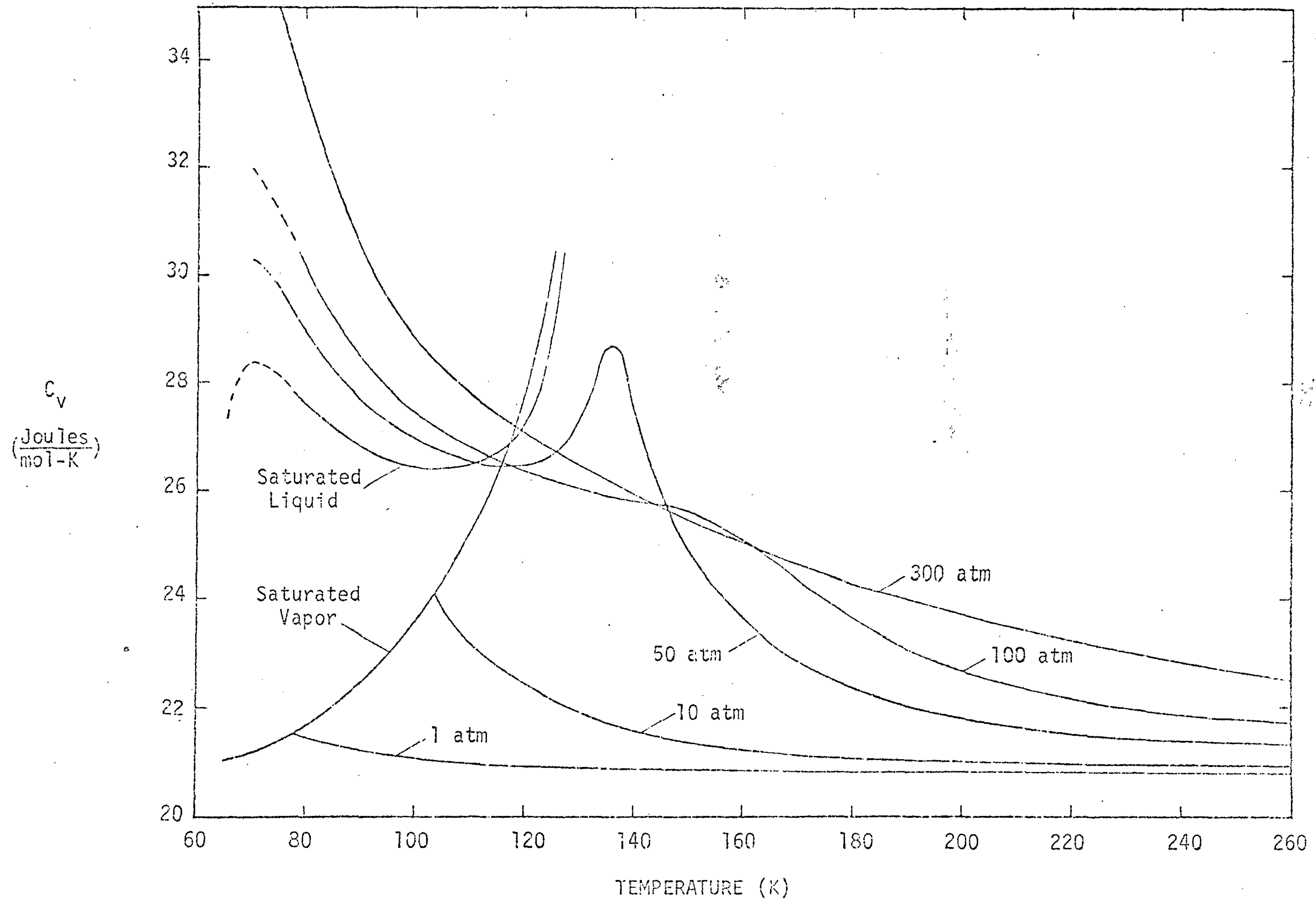


Figure 63 Constant Volume Heat Capacity (C_V) of Nitrogen Calculated with Equation of State (2) with Coefficients of Table IV

V. CONTINUING STUDIES

The coefficients reported in Tables III and IV are the results of least squares fits to the various data described in Section II. Studies are in progress to determine the location of the critical points for both fluids as represented by these equations, and to bring the reported vapor pressure equations and equations of state into accord at the critical point. Preliminary results suggest that a further study of the weighting of P-ρ-T data in the critical region and the inclusion of measured values of the density for the saturated liquid will result in an imporved fit of the data in that vicinity.

A study of properties of the liquid on the fusion line and comparison of the values represented by the equations of state to measured values will be continued. The triple point location will be reviewed to insure consistency among the vapor pressure equation, equation of state, and the melting curve representation.

The techniques of property calculation used in this work will be reviewed and the computer programs employed will be documented. Property tables will be calculated for both oxygen and nitrogen for applicable ranges of pressure and temperature. Extrapolations to higher temperatures and lower temperatures for the vapor will be included where appropriate. Extrapolations to the melting curve will also be made where measurements are available to establish their validity. Estimates of the accuracy of the tables will be given.

Comparisons with other measured thermodynamic data will be made to establish the consistency of the property formulation developed with the available experimental data. This will include comparisons to velocity of sound data, latent heat data, enthalpy data, Joule-Thompson coefficients, and the heat capacity at constant saturation.

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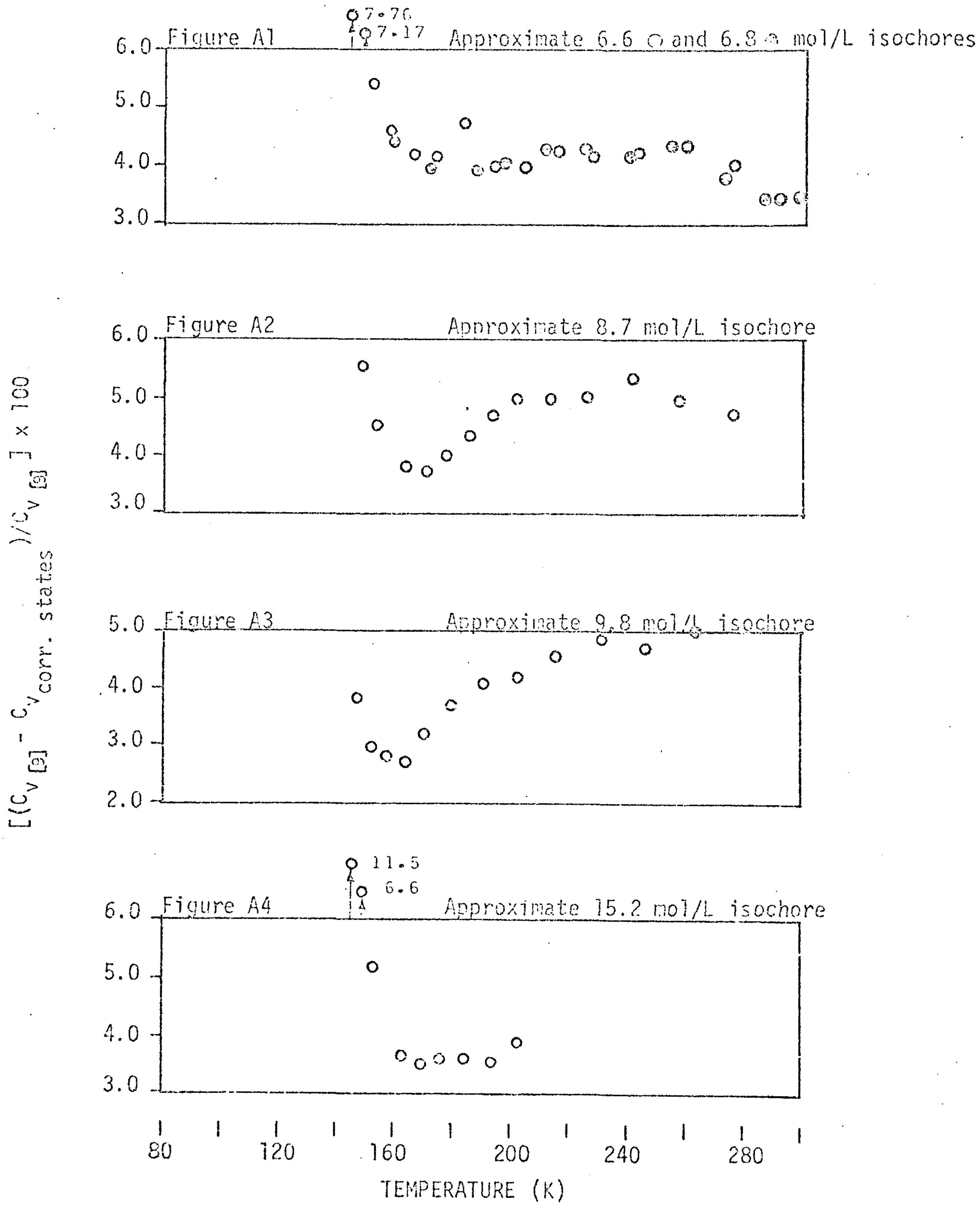
APPENDIX A

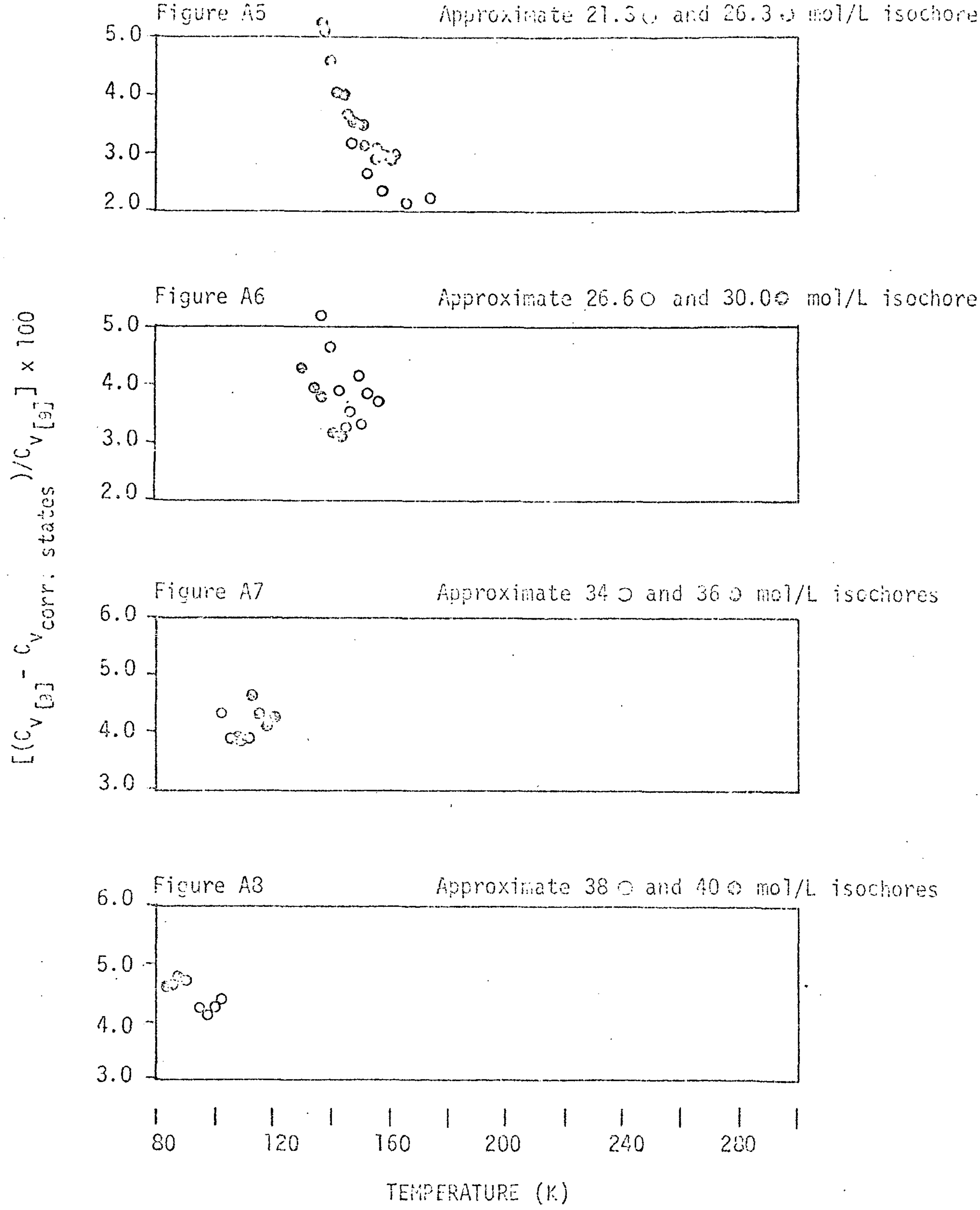
Heat Capacity Values Calculated Using the Principle of Corresponding States

In the determination of the equation of state for nitrogen as described in section II-C, the principle of corresponding states was used to calculate C_v values for nitrogen from the oxygen equation for C_v (equation 4) of [0-24], as suggested in [11].

To establish the validity of the corresponding states analysis employed in this work, the method described above was utilized in the calculation of C_v values for fluorine which were then compared to the experimental data of [9]. Critical parameters for fluorine were taken from [10]. Figures A1 through A8 show the results of this comparison.



Comparison of C_v Data for Fluorine from [9] with Values Predicted from Oxygen Equation of [O-24] using the Principle of Corresponding States



Comparison of C_v Data for Fluorine from [9] with Values Predicted from Oxygen Equation of [0-24] using the Principle of Corresponding States

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An Equation of State for Oxygen and Nitrogen II

R. B. Stewart, R. T. Jacobsen, and A. F. Myers,
University of Idaho, Engineering Experiment Station, Progress Report (January 1, 1972).

An error has been found in Table III, Coefficients for the Equation of State (2) for Oxygen. The value for N_{24} should be changed to,

$$N_{24} = -0.104770899761072 \times 10^{-1}.$$

The table (page 15) as printed gave the above value with the multiplier ... $\times 10^{1}$.

4A

R. B. Stewart

April 27, 1972