

# An Equation of State for Fluid Parahydrogen from the Triple-Point to 100 °K at Pressures to 350 Atmospheres

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This equation of state may be useful for interpolation and for computations which include thermodynamic properties of parahydrogen. A principal advantage is that it employs only one set of 24 coefficients for all fluid states. The basic form is relatively simple. An adjustment term for the critical region leads to good agreement with published PVT data and specific heats in this especially difficult area. The forms of fitting functions were developed by systematic trial methods using least squares to find the coefficients.

Key Words: Equation of state, hydrogen, parahydrogen, PVT-relations, thermodynamic properties.

## List of Symbols and Units

$A(\rho)$ ,  $B(\rho)$ ,  $C(\rho)$  density-dependent parameters.  
 $C_v$ , specific heat at constant volume;  $C_v^\circ$  for ideal gas states.  
 $d$ , density.  
 $d_c$ ,  $d_t$ , critical-point, and triple-point densities.  
 $\Delta_p \equiv (100/n) \cdot \sum_1^n |P/P_{\text{calc}} - 1|$  for  $n$  data.  
 $J$ , the joule.  
 $l$ , the liter, defined as 1000 cm<sup>3</sup> (12th Gen. Conf. Wts. Measures, Paris, October 1964).\*\*  
 $P$ , pressure.  
 $P_c$ ,  $P_t$ , critical-point, and triple-point pressures.  
 $P_t = 0.0695$  atm [6].  
 $\Pi(\rho)$ , a density-dependent, parametric pressure.  
 $R$ , the gas constant, 82.0597 cm<sup>3</sup> atm/g mol deg [3].  
 $\rho \equiv d/d_t$ , density reduced at the triple point.  
 $\sigma \equiv d/d_c$ , density reduced at the critical point.  
 $T$ , temperature, deg Kelvin (NBS 1955 low-temp. scale).  
 $T_c$ ,  $T_t$ , critical-point, and triple-point temperatures.  
 $\tau \equiv T/T_c$ , temperature reduced at the critical point.  
 $v \equiv 1/d$ , molal volume.  
 $x \equiv T/T_t$ , temperature reduced at the triple point.  
 $Y$ , a defined function of  $P$ ,  $\Pi$ ,  $T$ ,  $d$ .  
 $Z(\sigma, \tau)$ , a defined function.  
 $\varphi(\sigma, \tau)$ , a defined function.

## 1. Introduction

Our initial computations of thermodynamic properties of parahydrogen [1]<sup>1</sup> were accomplished by use of the Benedict-Webb-Rubin equation of state as modified by Strobridge [2]. To obtain the required accuracy, however, it was necessary to evaluate two sets of constants for two regions of the  $P$ - $V$ - $T$  surface. Serious computational complications then arose from the need to establish a practical continuity of thermodynamic properties over the boundaries of these regions. Partly for this reason, we used polynomial methods in our formal publication on the thermodynamic properties [3]. Despite these tabulations, there remains a need for an equation of state which can be used for interpolation, and for a multitude of computational investigations. A prerequisite of the following work has been that the equation of state shall require but a single set of constants for all fluid states of the substance (to avoid the above-mentioned problem of continuities).

Well-behaved descriptions of  $P$ - $\rho$ - $T$  behavior are obtained with the form  $P(\rho, T)$ , that is, with density and temperature as arguments or parameters. Density-dependence of specific heats then is obtained from  $P$ - $\rho$ - $T$  data via the thermodynamic relation,

$$(\partial C_v / \partial \rho)_T = (-T/\rho^2)(\partial^2 P / \partial T^2)_\rho.$$

Thus an exacting requirement upon any equation of state is to give the curvature of isochores,  $(\partial^2 P / \partial T^2)_\rho$ , accurately as a function of density and temperature.

We have elected to develop an isochoric form of equation, i.e., an expression for pressure in terms of

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<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

temperature. As any accurate equation for high densities must be empirical, we considered that temperature dependence along isochores (fixed mean intermolecular distance) probably would be less complicated than density-dependence along isotherms [4]. We have allowed the density-dependence of parameters in the equation to be given by  $P$ - $\rho$ - $T$  data on isochores. These data are interpolated from experimental isotherms [5].

## 2. The Behavior of $P$ - $\rho$ - $T$ Data on Isochores

In this section we survey the set of interpolated data on isochores with a view to discovering any useful generalities. This survey is possible because the experimental data on isotherms are dense, covering a wide range of conditions, and because they have been interpolated quite accurately on isochores [5]. For

convenience in obtaining derivatives for this survey, we take values computed from polynomial representations of the isochores with coefficients given by [3]. The derivatives therefore may be of low accuracy in some regions.

Plots of  $P$  versus  $T$  at constant density (isochores) appear to be a family of straight lines. (This emphasizes the need for extreme accuracy in  $P$ - $\rho$ - $T$  data used to obtain derivatives.) First derivatives  $(\partial P/\partial T)_\rho$ , however, reveal useful characteristics. Figure 1 gives dimensionless slopes,  $v \cdot (\partial P/\partial T)/R$ , versus  $T$  on isochores. For  $d > 0.013$  g mol/cm<sup>3</sup> each plot has a maximum, corresponding to an inflection in the  $P(T)$  relation. Curvatures,  $(\partial^2 P/\partial T^2)_\rho$ , are positive at low temperatures and negative at high temperatures. The locus of these inflections is important for the computation of specific heats on isotherms, due to the inversion of sign of the integrand. Figures 2 and 3 give the approximate  $P$ - $T$  and  $T$ - $\rho$  coordinates of the locus. On isotherms from 33 to about 52 °K we

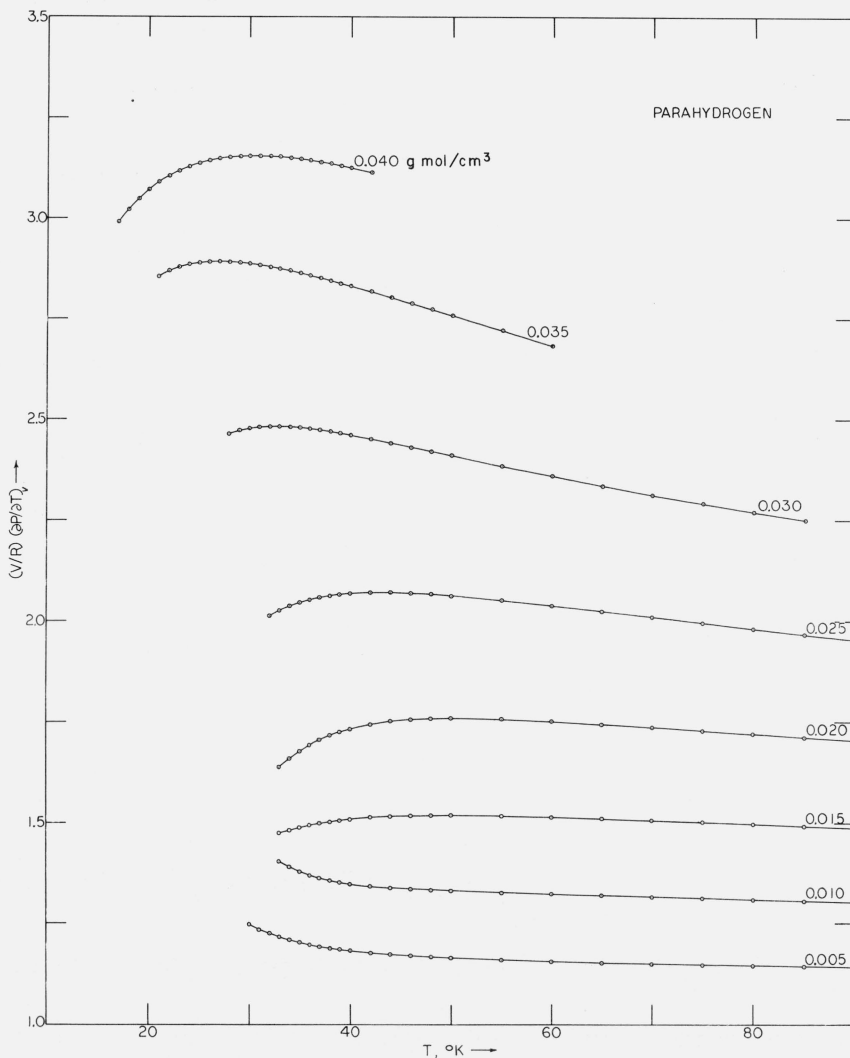


FIGURE 1. Slopes of selected isochores versus  $T$ .

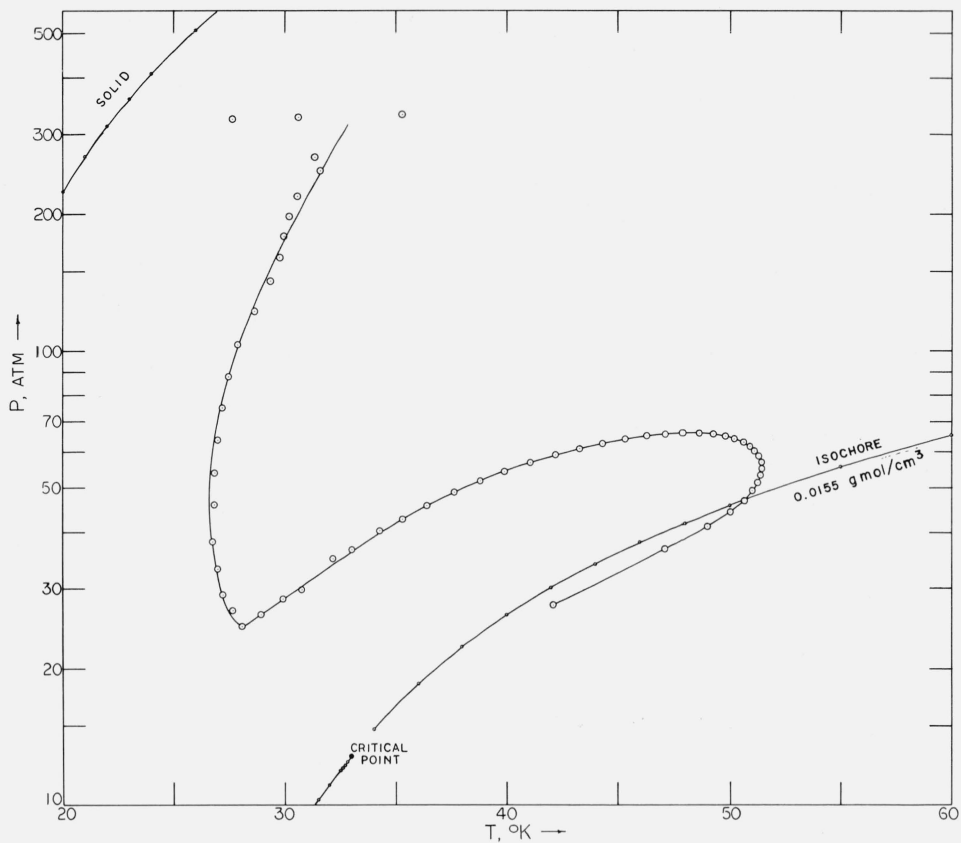


FIGURE 2. Locus of isochore inflection points in P-T coordinates.

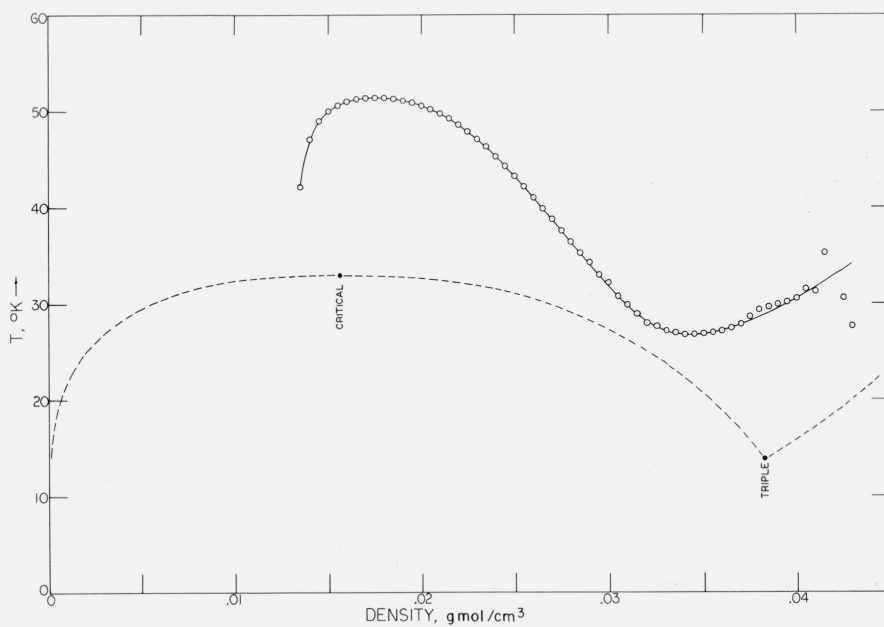


FIGURE 3. Locus of isochore inflection points in T-p coordinates.  
The dashed line from left to right represents saturated vapor, saturated liquid, and freezing liquid, respectively.

see that  $(\partial^2 P/\partial T^2)_\rho$  might have three inversions of sign as the density increases from zero to very high values. Part of this behavior already is known [16].

A further important characteristic of isochores is seen only by careful examination of differences in the data. The terminating ranges near saturation (low temperatures) exhibit sharp curvatures  $(\partial^2 P/\partial T^2)_\rho$  as  $T \rightarrow T_{\text{sat}}$ , appropriately named "hooks." In the critical region these curvatures are negative for  $\rho < \rho_c$  and positive for  $\rho > \rho_c$ .

### 3. A Preliminary Equation

We at first sought an elementary form for the sigmoid behavior of isochores. It should reduce to perfect gas behavior at low densities and also at high temperatures. We may include the purely density-dependent, parametric pressure found in the van der Waals and Beattie-Bridgeman equations, using the symbol  $\Pi(\rho)$  [4].

Assume that the inflection-point temperature,  $\theta(\rho)$ , is known for each isochore. For each, define a new temperature scale,  $t(\rho, T) \equiv T/\theta$ , and assume that  $\theta(0) = 0$ , (fig. 3). The simple form,

$$[P + \Pi(\rho)]/(R \cdot \theta \cdot d) = t \cdot \exp [(1-m)/(m \cdot t^m)],$$

with  $0 < m \neq 1$ , then yields a derivative,  $(\partial^2 P/\partial T^2)_\rho$ , which is positive for  $T < \theta$  and is negative for  $T > \theta$ .

Woolley et al., used an exponential form for hydrogen at high temperatures, omitting the term  $\Pi(\rho)$  [6]. We have, therefore, investigated the general form

$$\log_e Y = \sum_{i=1}^N A_i \cdot T^{-n_i}, \quad (1)$$

using the definition,

$$Y \equiv (P + \Pi)/(R \cdot T \cdot d).$$

One must discover necessary values for exponents,  $n_i$ , and the corresponding number of terms,  $N$ . Density-dependence of the  $A_i$  then is obtained from  $P(T)$  data by least squares under an iterative search for  $\Pi(\rho)$  on each isochore.

Lengthy investigations failed to yield a behavior for  $\Pi(\rho)$  which was sufficiently regular to permit analytical representation. With more than three terms (of the numerous powers in  $T$  investigated), the behavior of  $\Pi(\rho)$  and all  $A_i(\rho)$  was exceedingly irregular. With three terms, the behavior of  $\Pi(\rho)$  above 0.01 g mol/cm<sup>3</sup> was in rough accord with the Beattie-Bridgeman description, which we adopted for the constrained form of  $\Pi$ ,

$$\Pi(\rho) \equiv P_1 \cdot \rho^2 - P_2 \cdot \rho^3. \quad (2)$$

When  $P_1$  and  $P_2$  have been found (by iterative methods), the  $A_i$  have a regular dependence on  $\rho$ . The

lowest deviation,  $\Delta_p$  (see list of symbols), was obtained with the equation

$$\log_e Y = A \cdot \rho \cdot x^{-1/4} + B \cdot \rho \cdot x^{-1} + C \cdot x^{-3}. \quad (3)$$

where  $x \equiv T/T_i$ , and symbols  $A, B, C$ , replace the  $A_i$  of eq (1).

In each of the first two terms on the right one power of  $\rho$  has been introduced explicitly to diminish density-dependence of  $A$  and  $B$ . We note that exponent  $n_1 = 1/4$  is required for description of virial coefficients at low densities [7], and exponent  $n_3 = 3$  is found in the Beattie-Bridgeman equation. At sufficiently low densities, the term with  $n_2 = 1$  combines with  $\Pi(\rho)$ , independent of temperature. With  $P_1 = 703.2813$  atm and  $P_2 = 88.3125$  atm, one obtains the behavior for  $A(\rho), B(\rho), C(\rho)$  shown by figure 4.

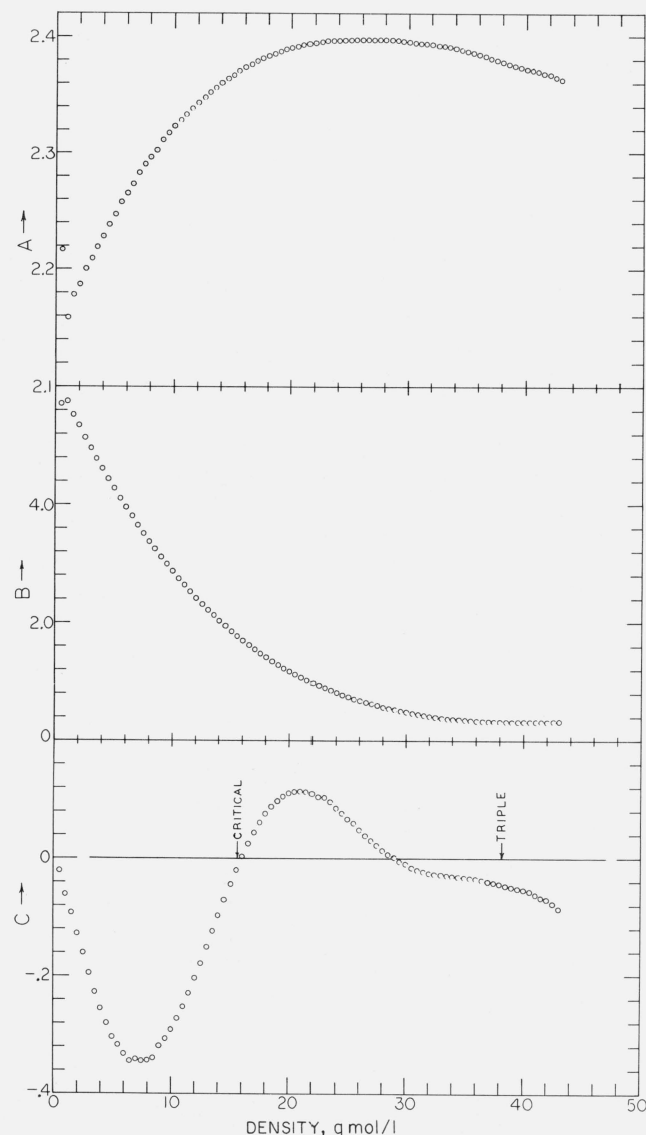


FIGURE 4. Parameters of eq (3),  $\Pi$  constrained.



Data needed for developing analytical descriptions of the parameters  $A(\rho)$ ,  $B(\rho)$ ,  $C(\rho)$  were obtained as described in appendix 6.1. The form of each description, given below, is the result of a considerable investigation, imposed by the need for high precision (appendix 6.2). In each, the number of terms and the values of exponents were explored systematically. In brief, the behaviors of figure 4 have been described as follows:

$$A(\rho) = A_1 + A_2 \cdot \rho \cdot \exp(-A_3 \cdot \rho), \quad (3-a)$$

$$B(\rho) = B_1 + \exp(B_2 + B_3 \cdot \rho + B_4 \cdot \rho^2 + B_5 \cdot \rho^4 + B_6 \cdot \rho^5), \quad (3-b)$$

$$C(\rho) = C_1 \cdot \rho + C_2 \cdot \rho^2 + C_3 \cdot \rho^3 + C_4 \cdot \rho^4 + C_5 \cdot \rho^5 + C_6 \cdot \rho^7 + C_7 \cdot \rho^{10} + C_8 \cdot \rho^{14}. \quad (3-c)$$

We found constants for eqs (3-a) to (3-c), omitting one datum at the lowest temperature (near saturation) from each of 85 isochores of interpolated data, 1.0

$\leq d \leq 43.0$  g mol/liter [5]. Mean deviation for the remaining 2002 points was  $\Delta_p = 0.026$  percent. Excessive deviations near the critical point, however, precluded calculation of specific heats in this region.

Anticipating an adjustment function for the critical region, we redetermined a set of 19 constants for eq (3), excluding an additional 59 data in the domain,  $32 \leq T \leq 35$  °K,  $8.5 \leq d \leq 22.5$  g mol/liter. The pressure was constrained at the liquid triple-point by means of a relatively small adjustment to the value of constant  $C_8$ .

These 19 constants,  $P_1, \dots, C_8$ , are given in table 1. Mean deviations for eq (3) appear in table 2, and individual deviations  $(P - P_{calc})/P_{calc}$  appear in table 3, given in parts per ten-thousand at temperatures through 42 °K. For higher temperatures they do not exceed a few parts in ten-thousand. (Where data do not exist, as in two-phase regions, or at  $P > 350$  atm, tables 3 and 5 contain zero entries.) Figure 5 gives the difference between left and right sides of eq (3), multiplied by  $10^4$ , on the 33-deg isotherm.

TABLE 1. Constants for eqs (3) and (4)

Equation (3)			Equation (4)		
Constant	Value		Constant	Value	
$T_t$ .....°K.....	13.803	[6]	$B_4$	-0.2410	0077
$T_c$ .....°K.....	32.976	[12]	$B_5$	1.8319	9451
$d_t$ .....g mol/cm <sup>3</sup> .....	(1/26.176)	[6]	$B_6$	-0.9445	7676
$P_1$ .....atm.....	697.0		$C_1$	-2.0176	0851
$P_2$ .....atm.....	81.0		$C_2$	-13.9844	7635
$A_1$ .....	2.1350	2896	$C_3$	128.3251	2808
$A_2$ .....	1.0170	4119	$C_4$	-294.2851	8710
$A_3$ .....	1.4268	4000	$C_5$	239.1130	5168
$B_1$ .....	-1.1427	1000	$C_6$	-67.1458	8122
$B_2$ .....	1.9682	3016	$C_7$	10.7210	8689
$B_3$ .....	-2.2337	9180	$C_8$	-0.7702	5591

Constant	Value	
$n$	8	
$d_c$ , g mol/cm <sup>3</sup>	0.0154	40
$C_8$	-0.7702	5578
$D_1$	.0004	5110
$D_2$	.0166	2606
$D_3$	-.0105	4950
$D_4$	7.28	
$E_1$	3.32	

TABLE 2. Mean deviations for eqs (3) and (4)

Equation number.....	(3)	(4)
Number of constants.....	19	19 + 6
No. of points used.....	<sup>a</sup> 1943	<sup>b</sup> 781
Value of exponent $n$ .....		8

No. of points for deviation	Mean deviation, $\Delta_p$ , %	
<sup>c</sup> 88	0.3576	0.0252
781	.....	.0456
1943	.0223	.....
2087	.0497	.0305

<sup>a</sup> One point omitted at lowest temperature of each of 85 isochores, and all points in domain,  $32 \leq T \leq 35$  °K,  $8.5 \leq d \leq 22.5$  g mol/liter.

<sup>b</sup> For the six constants in  $Z(\sigma, \tau)$ , data used in the domain,  $17 \leq T \leq 40$  °K,  $1.0 \leq d \leq 36.0$  g mol/liter.

<sup>c</sup> Points in the arbitrary critical domain,  $32 \leq T \leq 35$  °K,  $8.5 \leq d \leq 22.5$  g mol/liter.

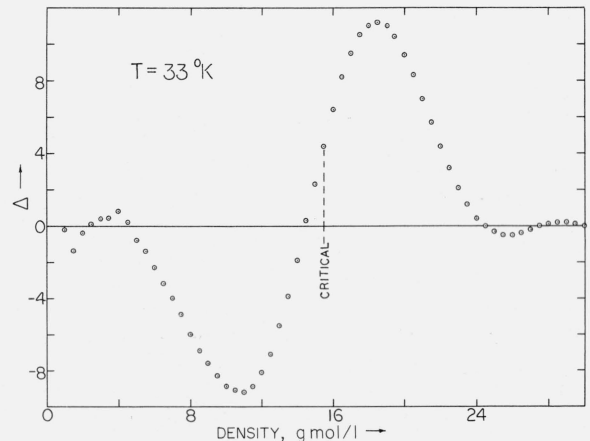


FIGURE 5. Difference between left and right sides of eq (3), multiplied by  $10^4$ , on 33-deg isotherm.

## 4. The Adjusted Equation

The deviation plot (fig. 5) shows behavior of an adjustment on isotherms which must be made to the preliminary equation in the critical region. We see that it may correspond at least to an incipient level spot or shelf in the  $P(\rho, T)$  surface in three-dimensions, and we should not expect the preliminary equation to describe this sharp irregularity. We have, therefore, added an adjustment term,  $Z(\sigma, \tau)$ , a function of reduced variables  $\sigma \equiv d/d_c$ ,  $\tau \equiv T/T_c$ , as follows,

$$\log_e Y = A \cdot \rho \cdot x^{-1/4} + B \cdot \rho \cdot x^{-1} + C \cdot x^{-3} + Z(\sigma, \tau). \quad (4)$$

The adjustment diminishes rapidly at densities away from the critical point, and at temperatures above the critical point.

Recent work suggests nonanalytic  $PVT$  behavior at the critical point, corresponding to a logarithmic infinity in  $C_v$  [8, 9, 10, 11]. The form of adjustment needed here, however, already is restricted by the preliminary equation of state. We have chosen an analytic form, with the justification that it describes the experimental facts quite well in the range investigated.

The form of  $Z$ , below, permits representation of the deviations in table 3 and also yields an acceptable set of specific heats in the critical region. With five coefficients  $D_1, \dots, E_1$  the function is

$$Z(\sigma, \tau) \equiv D(\sigma) \cdot \exp[-\phi(\sigma, \tau)], \quad (4-a)$$

$$D(\sigma) \equiv D_1 \cdot \sigma + (D_2 \cdot \sigma + D_3 \cdot \sigma^2) \cdot (\sigma - 1), \quad (4-b)$$

$$\phi(\sigma, \tau) \equiv D_4 \cdot (\sigma - 1)^2 + E_1 \cdot (\tau^n - 1). \quad (4-c)$$

We discuss briefly the basis for eq (4-a). Deviations at 33 deg (very near the critical isotherm at 32.976 deg) require at least a cubic polynomial in density, with roots at  $\sigma=0$ ,  $\sigma \approx 1$ ,  $\sigma > 1$ ; yet these deviations diminish rapidly at the highest densities. Equation (4-a) describes this behavior on isotherms. Temperature-dependence of these deviations is strong: when  $\tau=1.1$  the deviations have about vanished. For this reason we introduced the factor  $\exp(-E_1 \cdot \tau^n)$ . It gives the sharp isochore curvatures or "hooks" which contribute to calculated specific heats in the critical region. It also allows the calculated deviations to persist at temperatures below critical at densities near the saturation envelope.

On the right of eq (4-c) we selected the form of the first term,  $D_4 \cdot (\sigma - 1)^2$ , following some tedious work with the form  $D_4 \cdot (\sigma^m - 1)$ . Using the latter at  $m \approx 4$ , it was necessary to increase the powers of  $\sigma$  in eq (4-b) by two or more, e.g.,

$$D(\sigma) \approx D_1 \cdot \sigma^3 + (D_2 \cdot \sigma^4 + D_3 \cdot \sigma^5) \cdot (\sigma - 1),$$

to obtain a deviation,  $\Delta_p$ , comparable with that found via eq (4-b) above. Even so the magnitudes and the

signs of coefficients  $D_1, D_2, D_3$  exhibited radical behaviors, and we abandoned this search.

The constants of eq (4-a) have been determined for 781 data in the domain  $17 \leq T \leq 40$  °K;  $1.0 \leq d \leq 36.0$  g mol/liter, as described in section 5, below. Our general method was the following: We assumed values for exponent  $n$ , and then found  $D_4, E_1$  by iterative procedures which minimize  $\Delta_p$ . In every step we used  $D_1$  for constraint to the assigned critical-point pressure, and  $D_2, D_3$  to ensure that  $\partial P/\partial \sigma = \partial^2 P/\partial \sigma^2 = 0$  at the assigned critical point. (An estimate of  $n \approx 10$  at first was obtained by assuming that  $\exp[-E_1 \cdot (\tau^n - 1)] \approx 0.02$  at  $\tau=1.1$ , and that its maximum positive curvature shall occur near  $\tau=1$ .)

We have used the critical temperature established by Roder et al.,  $T_c = 32.976$  °K [12]. The critical pressure is computed at this temperature by means of the vapor-pressure equation of Weber et al., for accurate consistency,  $P_c = 12.759263$  atm [13]. The critical density has been varied within limits of uncertainty [14] to obtain consistency between specific heats from eq (4) and those tabulated in [3], as described below.

## 5. Examination of the Equation

An exacting test of the equation is behavior of calculated specific heats,  $C_v = C_v^o + C_v^*$ , where the "residual specific heat" is

$$C_v^* \equiv \text{const.} \cdot (-T) \cdot \int_0^\rho (\partial^2 P/\partial T^2)_\rho d\rho/\rho^2, \quad (5)$$

with  $\text{const.} = (0.101325 \text{ J/cm}^3 \text{ atm})/(d_i)$  when  $d_i$  is in g mol/cm<sup>3</sup>. As a rough guide, deviations within 5 to 10 percent of  $C_v$  often are considered satisfactory. In this work we use the tabulations of [3] for comparison, as they are in good agreement with experimental data.

We have varied parameters  $n$  and  $d_c$  of eq (4), examining behavior of the mean deviation  $\Delta_p$  and also of the mean deviation  $\Delta C_v$  between 470 specific heats from eq (4) and from [3]. Table 4(A) presents these results. In general, a minimum in  $\Delta_p$  does not coincide with the best minimum in  $\Delta C_v$ . We have made an arbitrary selection of  $n=8$ ,  $d_c = 15.44$  g mol/liter. Corresponding values for  $C_8, D_1, D_2, D_3, D_4$ , and  $E_1$  are given in table 1.

Table 5 presents residual specific heats from eq (4) with above constants and compares them with values from [3]. The first row at  $d=0$  gives  $C_v^o$  from [6]. At  $T < T_c$  the reference states for liquid are saturated liquid (not ideal gas), with properties given by table 6. Mean deviation for the 470 points of table 5 is 0.077 J/g mol deg, or roughly half of 1 percent. The greatest deviations are about 3 percent in neighborhood of the critical point.

It is interesting to see that integration on the 33 °K isotherm (within 0.02 °C of the critical point) yields satisfactory specific heats at the higher densities. Nevertheless, the maximum in  $C_v$  on this isotherm

Table 3. Individual relative deviations from eq (3).

DEVIATIONS OF PRESSURES ON ISOCHORES, PARTS PER TEN THOUSAND

T+K=	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	42
1.0	0	0	0	0	0	0	0	4	-1	2	-0	-1	-1	-1	-4	-2	-0	-2	0	-1	2	1	1	0	0
1.5	0	0	0	0	0	0	0	-2	2	1	1	3	-1	-0	-1	-2	-2	-1	-0	-1	1	0	0	0	0
2.0	0	0	0	0	0	0	0	0	0	1	1	1	1	-1	-1	-0	-1	-0	-1	0	1	1	0	1	1
2.5	0	0	0	0	0	0	0	0	0	0	0	1	2	0	0	1	0	-1	0	-1	0	1	1	0	1
3.0	0	0	0	0	0	0	0	0	0	0	0	-1	-0	1	1	1	1	0	1	0	0	1	1	2	1
3.5	0	0	0	0	0	0	0	0	0	0	0	-4	-2	1	-0	0	1	0	1	1	1	2	2	1	1
4.0	0	0	0	0	0	0	0	0	0	0	0	-8	-3	-2	-0	2	0	2	2	2	2	2	2	2	1
4.5	0	0	0	0	0	0	0	0	0	0	0	-4	-6	-1	0	1	0	1	2	2	2	2	3	2	2
5.0	0	0	0	0	0	0	0	0	0	0	0	0	0	-16	-10	-4	-2	1	2	2	2	3	2	2	2
5.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-17	-7	-3	0	2	3	3	3	2	3	2
6.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-25	-12	-6	-1	0	2	3	3	3	3	2
6.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-34	-18	-9	-2	-0	2	3	3	3	3	2
7.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-25	-12	-4	-1	1	3	3	3	4	4	2
7.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-34	-16	-7	-2	1	3	4	4	4	4	2
8.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-43	-21	-9	-3	1	3	4	4	4	4	2
8.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-53	-26	-12	-5	-0	3	3	4	4	4	2
9.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-31	-15	-6	-1	2	4	4	4	4	4	2
9.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-36	-18	-7	-1	1	4	4	4	4	4	2
10.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-42	-20	-8	-2	2	3	4	4	4	4	2
10.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-44	-22	-8	-2	1	3	4	4	4	4	2
11.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-50	-22	-8	-2	1	3	5	4	4	4	2
11.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-51	-22	-8	-2	1	3	4	4	4	4	2
12.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-50	-20	-7	-2	1	3	4	4	4	4	2
12.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-47	-17	-5	-1	1	3	4	4	4	4	2
13.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-39	-13	-4	-0	1	2	3	3	3	3	2
13.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-29	-8	-2	0	1	2	2	2	2	2	2
14.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-15	-2	-0	1	1	2	2	2	2	2	2
14.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	4	3	2	1	1	1	1	1	1	2
15.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	21	11	5	2	1	0	0	0	0	0	2
15.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	43	18	8	3	0	-1	-1	-0	1	-0	1
16.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	65	26	10	3	0	-1	-2	-1	-1	-0	1
16.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	87	32	12	3	-0	-2	-3	-2	-2	-0	1
17.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	107	38	13	3	-1	-3	-4	-3	-3	-0	1
17.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	125	43	14	3	-1	-3	-4	-4	-4	-1	1
18.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	138	46	15	3	-2	-4	-5	-5	-5	-1	1
18.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	148	48	15	2	-2	-4	-5	-5	-5	-2	1
19.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	151	49	15	2	-3	-5	-5	-6	-6	-2	1
19.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	148	48	14	1	-3	-5	-5	-6	-6	-2	1
20.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	141	45	13	-0	-4	-5	-5	-6	-6	-2	1
20.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	120	41	11	-1	-4	-5	-5	-6	-6	-2	1
21.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	112	38	10	-2	-5	-5	-6	-6	-6	-2	1
21.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	94	30	8	-2	-5	-4	-4	-4	-4	-1	1
22.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	74	24	6	-3	-4	-4	-3	-3	-3	-1	1
22.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	54	18	4	-3	-4	-3	-2	-2	-2	-0	1
23.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	120	36	12	2	-3	-3	-2	-1	-0	1	1
23.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	89	20	7	1	-2	-2	-1	0	1	2	2
24.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	60	8	2	-1	-2	-1	0	1	2	3	3
24.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	36	-0	-2	-1	-1	-0	1	2	3	4	4
25.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	18	-6	-4	-2	-1	1	2	3	5	5	5
25.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	5	-8	-6	-2	0	2	3	4	5	6	6
26.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	12	-4	-7	-6	-2	1	3	4	5	6	6
26.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-6	-8	-5	-6	-2	2	4	5	5	6	6
27.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-16	-10	-7	-5	-1	2	4	5	5	6	6
27.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-14	-19	-9	-0	-4	-1	3	5	5	6	6
28.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-24	-18	-8	1	-3	-1	3	5	5	6	6
28.5	0	0	0	0	0	0	0	0	0	0	0	0	0	-41	-26	-16	-6	2	-0	3	5	5	6	6	4
29.0	0	0	0	0	0	0	0	0	0	0	0	0	0	-30	-22	-12	-4	2	-1	0	3	4	5	4	3
29.5	0	0	0	0	0	0	0	0	0	0	0	0	0	-78	-20	-18	-9	-3	1	-1	3	4	4	3	3
30.0	0	0	0	0	0	0	0	0	0	0	0	0	0	-46	-13	-13	-5	-2	0	1	2	3	4	3	3
30.5	0	0	0	0	0	0	0	0	0	0	0	-120	-25	-7	-7	-4	-2	-1	-0	1	2	2	3	2	1
31.0	0	0	0	0	0	0	0	0	0	0	0	-45	-12	-3	-3	-2	-2	-3	-1	1	2	3	2	1	0
31.5	0	0	0	0	0	0	0	0	0	-114	-13	-4	-0	-0	-2	-3	-4	-1	0	1	1	2	1	1	-0
32.0	0	0	0	0	0	0	0	-252	-36	2	1	1	2	-2	-3	-5	-1	-0	0	2	1	0	0	-1	-0
32.5	0	0	0	0	0	0	0	-69	-7	7	4	2	2	-2	-4	-5	-2	-1	-0	-0	1	1	0	-0	-1
33.0	0	0	0	0	0	0	-102	-19	4	8	4	2	3	-3	-4	-5	-2	-1	-1	-0	1	1	0	-0	-1
33.5	0	0	0	0	0	-113	-26	-1	8	8	4	1	2	-3	-5	-4	-3	-1	-1	-1	1	0	1	-0	-0
34.0	0	0	0	0	0	-27	-5	6	8	6	4	1	1	-3	-4	-3	-3	-1	-1	-1	1	0	1	0	-1
34.5	0	0	0	0	0	56	-5	3	8	7	3	3	-0	-0	-3	-4	-2	-3	-1	-1	-1	1	1	1	1
35.0	0	0	0	0	97	29	3	5	7	5	2	2	-1	-2	-3	-4	-1	-3	-1	-1	-0	1	1	2	2
35.5	0	0	0	248	22	12	6	5	5	3	0	1	-1	-2	-3	-3	-0	-2	-1	-0	-0	1	1	2	2
36.0	0	0	197	48	2	0	5	4	4	2	-0	0	-1	-3	-2	-2	-0	-2	-1	0	0	1	1	2	2
36.5	0	47	-7	-4	-6	-6	4	3	2	1	-1	0	-1	-3	-2	-2	0	-1	-1	0	1	1	1	2	2
37.0	-149	-59	-31	-22	-9	-8	2	2	1	1	-0	0</													

TABLE 4. Effects of parameters in eq (4)  
Part A,  $T_c = 32.976$  °K

$d_c$ , g mol/l	$(\Delta p, \%) \cdot 100$			$\Delta C_p$ , J/mol deg
	88 <sup>a</sup>	781 <sup>b</sup>	2087 <sup>c</sup>	
				470 <sup>d</sup>
15.40	3.05	4.37	2.97	0.106
15.42	2.51	4.45	3.00	.092
15.44	2.99	4.54	3.04	.089
15.36	2.68	4.47	3.01	.104
15.38	2.38	4.40	2.99	.092
15.40	2.32	4.40	2.99	.086
15.42	2.36	4.47	3.01	.079
15.44	2.52	4.56	3.05	.077
15.46	2.70	4.67	3.09	.078
15.36	2.90	4.54	3.04	.094
15.38	2.52	4.46	3.01	.089
15.40	2.41	4.46	3.01	.092
15.42	2.32	4.54	3.04	.095
15.44	2.41	4.62	3.07	.098
15.46	2.43	4.72	3.11	.106

TABLE 4. Effects of parameters in eq (4) (continued)  
Part B,  $n = 8$

$T_c$ , deg K	$d_c$ , g mol/l	$(\Delta p, \%) \cdot 100$			$\Delta C_p$ , J/mol deg
		88 <sup>a</sup>	781 <sup>b</sup>	2087 <sup>c</sup>	
32.982	15.40	2.51	4.41	2.99	0.086
32.982	15.44	2.60	4.57	3.05	.076
32.982	15.48	3.11	4.78	3.13	.083
32.984	15.43	2.59	4.51	3.03	.077
32.984	15.44	2.67	4.56	3.05	.075
32.984	15.45	2.74	4.61	3.07	.076
32.984	15.46	2.88	4.67	3.09	.077
32.986	15.40	2.55	4.42	2.99	.086
32.986	15.44	2.69	4.56	3.05	.076
32.986	15.48	3.24	4.78	3.13	.082
32.990	15.40	2.74	4.43	3.00	.088
32.990	15.44	2.88	4.56	3.05	.079
32.990	15.48	3.50	4.78	3.13	.079

<sup>a</sup> 88 Points,  $32 \leq T \leq 35$  °K,  $8.5 \leq d \leq 22.5$  g mol/liter.

<sup>b</sup> 781 Points,  $17 \leq T \leq 40$ ,  $1.0 \leq d \leq 36.0$ .

<sup>c</sup> 2087 Points,  $17 \leq T \leq 100$ ,  $1.0 \leq d \leq 43.0$ .

<sup>d</sup> 470 Values of  $C_p$ , [3] and table 5.

Table 5. Calculated specific heats from eq (4) with  $n = 8$ ,  $d_c = 15.44$  g mol/l<sup>†</sup>

DENSITY GMOL/L	SPECIFIC HEAT AT CONSTANT VOLUME, JOULE/GMOL DEG.													
	TEMPERATURE, DEG.K													
	30.00		31.00		32.00		33.00		34.00		35.00		36.00	
0.000	CALCD	REFER	CALCD	REFER	CALCD	REFER	CALCD	REFER	CALCD	REFER	CALCD	REFER	CALCD	REFER
	12.47	12.47	12.47	12.47	12.47	12.47	12.47	12.47	12.47	12.47	12.47	12.47	12.47	12.47
1.000	0.35	0.31	0.33	0.29	0.30	0.28	0.28	0.27	0.26	0.25	0.24	0.24	0.23	0.22
2.000	0.75	0.70	0.69	0.66	0.64	0.62	0.59	0.58	0.55	0.53	0.50	0.49	0.47	0.45
3.000	1.18	1.17	1.10	1.09	1.02	1.01	0.93	0.95	0.86	0.85	0.78	0.76	0.72	0.68
4.000	1.65	1.73	1.54	1.59	1.43	1.47	1.31	1.37	1.19	1.20	1.08	1.06	0.98	0.93
5.000	2.15	2.37	2.02	2.16	1.89	1.98	1.72	1.85	1.55	1.58	1.38	1.37	1.24	1.19
6.000	0.00	0.00	2.56	2.80	2.41	2.55	2.19	2.37	1.94	2.00	1.70	1.70	1.50	1.46
7.000	0.00	0.00	0.00	0.00	3.01	3.19	2.74	2.95	2.39	2.45	2.04	2.06	1.76	1.74
8.000	0.00	0.00	0.00	0.00	3.72	3.70	3.38	3.60	2.89	2.96	2.40	2.35	2.01	2.02
9.000	0.00	0.00	0.00	0.00	0.00	0.00	4.11	4.33	3.45	3.44	2.78	2.66	2.26	2.30
10.000	0.00	0.00	0.00	0.00	0.00	0.00	4.91	4.89	4.05	3.89	3.16	2.99	2.48	2.55
11.000	0.00	0.00	0.00	0.00	0.00	0.00	5.74	5.50	4.65	4.37	3.53	3.33	2.68	2.76
12.000	0.00	0.00	0.00	0.00	0.00	0.00	6.48	6.16	5.19	4.85	3.84	3.63	2.84	2.92
13.000	0.00	0.00	0.00	0.00	0.00	0.00	7.03	6.81	5.58	5.28	4.06	3.82	2.93	3.01
14.000	0.00	0.00	0.00	0.00	0.00	0.00	7.27	7.26	5.74	5.54	4.14	3.88	2.95	3.02
15.000	0.00	0.00	0.00	0.00	0.00	0.00	7.15	7.36	5.64	5.55	4.05	3.80	2.87	2.95
16.000	0.00	0.00	0.00	0.00	0.00	0.00	6.66	7.16	5.27	5.28	3.81	3.32	2.77	2.62
17.000	0.00	0.00	0.00	0.00	0.00	0.00	5.86	6.36	4.68	4.71	3.43	2.99	2.50	2.41
18.000	0.00	0.00	0.00	0.00	0.00	0.00	4.88	5.23	3.95	3.94	2.98	2.59	2.24	2.17
19.000	0.00	0.00	0.00	0.00	0.00	0.00	3.86	3.98	3.20	3.09	2.50	2.18	1.97	1.89
20.000	0.00	0.00	0.00	0.00	0.00	0.00	2.91	2.79	2.50	2.29	2.05	1.79	1.71	1.61
21.000	0.00	0.00	0.00	0.00	0.00	0.00	2.13	1.83	1.91	1.63	1.67	1.46	1.47	1.35
22.000	0.00	0.00	0.00	0.00	0.00	0.00	1.54	1.42	1.46	1.31	1.37	1.23	1.28	1.15
23.000	0.00	0.00	0.00	0.00	-0.07	-0.05	1.12	1.17	1.14	1.10	1.14	1.05	1.17	1.00
24.000	0.00	0.00	0.00	0.00	-0.38	-0.29	0.85	0.97	0.93	0.93	0.98	0.90	1.00	0.87
25.000	0.00	0.00	0.00	0.00	-0.58	-0.48	0.68	0.81	0.79	0.79	0.87	0.79	0.92	0.78
26.000	0.00	0.00	-0.13	-0.16	-0.70	-0.63	0.58	0.69	0.70	0.69	0.80	0.70	0.86	0.71
27.000	-0.03	-0.04	-0.22	-0.29	-0.77	-0.74	0.52	0.60	0.65	0.62	0.75	0.65	0.82	0.67
28.000	-0.11	-0.15	-0.28	-0.39	-0.82	-0.81	0.49	0.54	0.62	0.58	0.73	0.62	0.81	0.66
29.000	-0.17	-0.23	-0.32	-0.44	-0.84	-0.85	0.47	0.52	0.62	0.57	0.73	0.62	0.81	0.66
30.000	-0.20	-0.27	-0.34	-0.47	-0.84	-0.86	0.48	0.52	0.63	0.58	0.75	0.64	0.83	0.69
31.000	-0.21	-0.28	-0.33	-0.47	-0.83	-0.85	0.49	0.53	0.65	0.60	0.77	0.67	0.86	0.72
32.000	-0.20	-0.27	-0.32	-0.45	-0.81	-0.83	0.52	0.57	0.68	0.64	0.81	0.71	0.90	0.77
33.000	-0.19	-0.25	-0.30	-0.42	-0.78	-0.80	0.56	0.60	0.72	0.68	0.86	0.76	0.95	0.82
34.000	-0.16	-0.23	-0.27	-0.39	-0.75	-0.76	0.60	0.65	0.77	0.73	0.91	0.81	1.00	0.87
35.000	-0.14	-0.20	-0.24	-0.36	-0.71	-0.72	0.64	0.69	0.81	0.77	0.95	0.85	1.06	0.92
36.000	-0.12	-0.18	-0.21	-0.33	-0.68	-0.69	0.68	0.72	0.86	0.81	1.00	0.90	1.11	0.97
37.000	-0.10	-0.17	-0.19	-0.31	-0.65	-0.67	0.71	0.75	0.90	0.85	1.05	0.94	1.16	1.02
38.000	-0.09	-0.16	-0.17	-0.30	-0.63	-0.64	0.74	0.78	0.93	0.88	1.09	0.98	1.20	1.06
39.000	-0.09	-0.16	-0.16	-0.29	-0.61	-0.63	0.76	0.80	0.96	0.91	1.17	1.01	1.24	1.10
40.000	-0.09	-0.16	-0.16	-0.29	-0.60	-0.62	0.78	0.82	0.98	0.93	1.15	1.04	1.27	1.14
41.000	-0.11	-0.16	-0.16	-0.29	-0.60	-0.62	0.79	0.83	0.99	0.94	1.17	1.06	1.30	1.15
42.000	-0.12	-0.18	-0.18	-0.30	-0.61	-0.62	0.78	0.82	1.00	0.94	1.18	1.00	1.31	1.00

Table 5. (continued)

DENSITY GMOL/L	SPECIFIC HEAT AT CONSTANT VOLUME, JOULE/GMOL DEG.															
	40.00		50.00		60.00		70.00		80.00		90.00		100.00			
	CALCD	REFR	CALCD	REFR	CALCD	REFR	CALCD	REFR	CALCD	REFR	CALCD	REFR	CALCD	REFR		
0.000	12.49	12.49	12.64	12.64	13.09	13.09	13.99	13.99	15.31	15.31	16.94	16.94	18.69	18.69		
1.000	0.18	0.18	0.12	0.12	0.09	0.09	0.08	0.06	0.07	0.06	0.06	0.05	0.06	0.04		
2.000	0.36	0.35	0.24	0.24	0.18	0.18	0.15	0.13	0.13	0.11	0.12	0.10	0.12	0.08		
3.000	0.55	0.51	0.35	0.35	0.26	0.27	0.22	0.20	0.20	0.17	0.18	0.14	0.17	0.12		
4.000	0.74	0.66	0.46	0.44	0.34	0.35	0.29	0.27	0.26	0.22	0.24	0.18	0.23	0.15		
5.000	0.92	0.80	0.56	0.53	0.42	0.43	0.35	0.33	0.32	0.27	0.29	0.23	0.28	0.19		
6.000	1.09	0.93	0.66	0.61	0.49	0.51	0.41	0.39	0.37	0.32	0.35	0.27	0.33	0.22		
7.000	1.24	1.05	0.75	0.68	0.56	0.58	0.47	0.45	0.42	0.37	0.40	0.31	0.38	0.25		
8.000	1.38	1.21	0.83	0.75	0.62	0.63	0.52	0.50	0.47	0.42	0.45	0.37	0.43	0.32		
9.000	1.49	1.38	0.89	0.81	0.67	0.67	0.57	0.54	0.52	0.47	0.50	0.43	0.48	0.40		
10.000	1.58	1.51	0.95	0.86	0.72	0.70	0.62	0.57	0.57	0.52	0.54	0.49	0.53	0.48		
11.000	1.63	1.62	0.99	0.90	0.76	0.73	0.66	0.61	0.62	0.57	0.59	0.56	0.58	0.56		
12.000	1.67	1.69	1.02	0.92	0.79	0.75	0.70	0.64	0.66	0.61	0.64	0.61	0.63	0.63		
13.000	1.67	1.73	1.04	0.94	0.82	0.78	0.74	0.67	0.71	0.66	0.69	0.67	0.68	0.69		
14.000	1.66	1.72	1.05	0.95	0.85	0.80	0.78	0.71	0.75	0.70	0.74	0.72	0.73	0.76		
15.000	1.62	1.68	1.05	0.96	0.87	0.82	0.81	0.74	0.79	0.74	0.78	0.77	0.78	0.81		
16.000	1.56	1.62	1.04	0.95	0.90	0.84	0.85	0.78	0.84	0.79	0.84	0.82	0.83	0.86		
17.000	1.49	1.52	1.03	0.95	0.92	0.87	0.89	0.82	0.88	0.83	0.89	0.86	0.89	0.91		
18.000	1.41	1.40	1.02	0.94	0.94	0.90	0.93	0.86	0.93	0.87	0.94	0.91	0.95	0.95		
19.000	1.32	1.28	1.01	0.93	0.96	0.93	0.97	0.90	0.98	0.92	1.00	0.96	1.01	1.00		
20.000	1.24	1.16	1.01	0.93	0.99	0.96	1.01	0.94	1.04	0.97	1.06	1.01	1.07	1.05		
21.000	1.16	1.05	1.00	0.93	1.02	1.00	1.06	0.99	1.09	1.02	1.12	1.06	1.13	1.11		
22.000	1.08	0.96	1.00	0.93	1.05	1.04	1.11	1.05	1.15	1.08	1.18	1.13	1.20	1.17		
23.000	1.02	0.88	1.01	0.94	1.09	1.08	1.16	1.10	1.22	1.15	1.25	1.19	1.27	1.24		
24.000	0.97	0.82	1.03	0.96	1.14	1.13	1.22	1.16	1.28	1.21	1.32	1.26	1.35	1.32		
25.000	0.94	0.79	1.05	0.99	1.19	1.18	1.29	1.23	1.35	1.28	1.40	1.34	1.42	1.40		
26.000	0.92	0.77	1.09	1.03	1.25	1.24	1.36	1.30	1.43	1.36	1.47	1.42	1.50	1.49		
27.000	0.91	0.77	1.13	1.07	1.31	1.30	1.43	1.37	1.51	1.44	1.56	1.51	1.58	1.58		
28.000	0.93	0.78	1.19	1.13	1.38	1.37	1.51	1.45	1.59	1.52	1.64	1.60	1.67	0.00		
29.000	0.95	0.82	1.25	1.19	1.46	1.45	1.60	1.53	1.68	1.61	1.73	1.69	1.76	0.00		
30.000	0.99	0.86	1.32	1.26	1.54	1.53	1.68	1.62	1.77	1.70	1.82	0.00	1.85	0.00		
31.000	1.04	0.91	1.39	1.33	1.63	1.61	1.78	1.71	1.86	1.81	1.92	0.00	1.94	0.00		
32.000	1.10	0.97	1.47	1.41	1.72	1.70	1.87	1.81	1.96	0.00	2.01	0.00	2.04	0.00		
33.000	1.16	1.04	1.56	1.49	1.81	1.79	1.97	1.92	2.06	0.00	2.11	0.00	2.14	0.00		
34.000	1.23	1.10	1.64	1.58	1.91	1.89	2.07	0.00	2.16	0.00	2.21	0.00	2.24	0.00		
35.000	1.30	1.16	1.73	1.66	2.00	2.00	2.17	0.00	2.26	0.00	2.31	0.00	2.34	0.00		
36.000	1.36	1.23	1.82	1.75	2.10	0.00	2.27	0.00	2.36	0.00	2.42	0.00	2.44	0.00		
37.000	1.43	1.29	1.90	1.85	2.20	0.00	2.37	0.00	2.47	0.00	2.52	0.00	2.55	0.00		
38.000	1.49	1.35	1.99	1.96	2.29	0.00	2.47	0.00	2.57	0.00	2.62	0.00	2.65	0.00		
39.000	1.54	1.42	2.07	0.00	2.39	0.00	2.57	0.00	2.67	0.00	2.73	0.00	2.75	0.00		
40.000	1.59	0.00	2.15	0.00	2.48	0.00	2.67	0.00	2.78	0.00	2.83	0.00	2.86	0.00		
41.000	1.64	0.00	2.22	0.00	2.57	0.00	2.77	0.00	2.88	0.00	2.94	0.00	2.96	0.00		
42.000	1.67	0.00	2.29	0.00	2.65	0.00	2.86	0.00	2.98	0.00	3.04	0.00	3.06	0.00		

FOR 470 POINTS, MEAN = 0.077 J/GMOL DEG.

† At  $T < T_c$  the reference states for liquid are the saturated liquid (not ideal gas) with properties given by table 6.

TABLE 6. Properties of saturated liquid used in the specific heat calculations

$T$ , °K	$d$ , g mol/liter [15]	$C_c$ , J/g mol deg [3]
30.0	26.753	13.07
31.0	25.103	13.33
32.0	22.825	13.79

near  $d = 14.0$  g mol/liter may be an imperfection, even though it is consistent with the estimated sign inversion of  $(\partial^2 P / \partial T^2)$  near 13.0 g mol/liter at 33 °K (fig. 3). This could be the subject of another, lengthy investigation, which might include adjustment of data for gravitational effects, nonanalytic functions, etc. [8].

Further to validate the behavior of eq (4), we have made the following examinations. (1) A table of relative deviations, similar to table 3 in this report, shows that they are comparable in the critical region with those elsewhere, and that many near the saturation envelope at  $T < T_c$  have been appreciably diminished relative to table 3. (2) A table of pressures and derivatives  $\partial P / \partial \rho$ ,  $\partial^2 P / \partial \rho^2$  on the critical isotherm shows that  $\partial P / \partial \rho \geq 0$ , and that  $\partial^2 P / \partial \rho^2 \leq 0$  as  $\rho \leq \rho_c$ . Dif-

ferences in  $\partial^2 P / \partial \rho^2$  give the estimate  $\partial^3 P / \partial \rho^3 = 9.0$  atm at  $\rho_c$  (where  $\rho \equiv d/d_i$ ). (3) A table of calculated pressures at all  $\rho$ ,  $T$  arguments of the interpolated data [5] shows monotonic increase of  $P$  with either  $\rho$  or  $T$  in single-phase regions. (4) A table of calculated densities of the saturated vapor and liquid phases, and of the freezing liquid phase, shows acceptable agreement with previously derived results [15].

In conclusion, we mention a further examination of eq (4-a). Effects of varying  $T_c$  ( $P_c$  obtained from [13]) are in table 4(B). We do not feel that these results justify a change of  $T_c$  from [12]. Constants corresponding to the minimum deviation,  $\Delta C_v = 0.075$  J/g mol deg, nevertheless are given in table 7 because the critical point constants are close to those determined initially by Hoge and Lassiter, namely  $T_c = 32.984 \pm 0.02$  °K,  $d_c = 15.27 \pm 0.30$  g mol/liter,  $P_c = 12.77 \pm 0.04$  atm [14].

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TABLE 7. Constants for alternate  $T_c$   
Equation (4-a)

Constant	Value
$n$ .....	8
$T_c$ .....°K.....	32.984
$d_c$ .....g mol/liter.....	15.44
$P_c$ , [13].....atm.....	12.774 257
$C_8$ .....	-0.7702 5576
$D_1$ .....	.0004 4993
$D_2$ .....	.0161 4536
$D_3$ .....	-.0102 2498
$D_4$ .....	7.22
$E_1$ .....	3.32

routine in machine language. Mrs. Levelt Sengers kindly suggested improvements in the manuscript and encouraged us to seek a form which would be non-analytic at the critical point.

## 6. Appendixes

### 6.1. Method Used To Find Data for $A(\rho)$ , $B(\rho)$ , $C(\rho)$

With reference to eq (3) and determination of coefficients on the right side by least squares on isochores, we used a method whereby deviations introduced by the arbitrary form of the first coefficient,  $A(\rho)$ , will appear in data for the second coefficient,  $B(\rho)$ , and so forth. After adjusting the constants in  $A(\rho)$  we used its representation on the left side, and redetermined data for  $B$  and for  $C$  by least squares on isochores in the transposed form,

$$\{\log Y - A_{\text{calc}} \cdot \rho \cdot x^{-1/4}\} = B \cdot \rho \cdot x^{-1} + C \cdot x^{-3},$$

and so forth.

### 6.2. The Requirement for High Precision in $A(\rho)$ , Etc.

The explicit form of eq (3) for pressure,

$$P = -\Pi(\rho) + F(\rho, T)$$

shows that  $P$  is obtained as a difference of two principal terms. At high densities the value of  $\Pi$  may exceed 700 atm. At high densities and low temperatures the value of  $P$  may be as low as 0.0695 atm (triple

point). Values for the parameters  $A(\rho)$ ,  $B(\rho)$ , etc., therefore may be required with a precision ten thousand-fold greater than desired in the calculated pressure.

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