

# Formulation of a Nonanalytic Equation of State for Parahydrogen\*

Robert D. Goodwin\*\*

Institute for Basic Standards, National Bureau of Standards, Boulder, Colorado 80302

(July 15, 1969)

A method is described for building an equation of state which gives an infinite specific heat  $C_v$  at the critical point approached from the one-phase domain. Interpolated  $PVT$  data are used on isochores up to 100 K at densities to the liquid triple point. In addition to an accurate representation of these data, the equation gives specific heats which agree well with experimental data along near-critical isochores.

Key words: Critical point; equation of state; hydrogen; parahydrogen; specific heats; thermodynamic properties.

## Symbols and Units

(Subscripts  $c$  and  $t$  refer to critical and liquid triple points)

$A, B, C, D,$	density-dependent coefficients of eq (5).
$C_v(\rho, T),$	specific heat, J/mol K.
$C_v^0(T),$	specific heat at $\rho=0$ , J/mol K.
$C_v^*(\rho, T),$	interaction specific heat, J/mol K.
$d,$	density.
$d_c,$	15.59 mol/l for eq (3), [13].
$d_t,$	(1.0/0.026176) mol/l, [19].
$J,$	the joule.
$l,$	the liter.
mol,	the gram mole, based on $R$ in this work [5].
$P,$	pressure, 1 atm = 0.101325 MN/m <sup>2</sup> .
$R,$	the gas constant, 0.0820597 l-atm/(mol-deg) [5].
$\rho \equiv d/d_t,$	density reduced at the liquid triple point.
$\sigma \equiv d/d_c,$	density reduced at the critical point.
$T,$	temperature K, (NBS 1955).
$T_c,$	32.93 K.
$T_t,$	13.803 K, [19].
$T_s(\rho),$	coexistence temperature, K.
$\theta(\rho),$	a locus of temperatures, K.
$v,$	1/ $d$ , molal volume.
$\omega(\rho, T) \equiv$	1 - $\theta(\rho)/T$ .
$x \equiv T/T_t,$	temperature reduced at the triple point.
$Z \equiv Pv/RT,$	the "compressibility factor".

## 1. Introduction

The objective of this work is an accurate form of an equation of state to replace costly approximation methods in the computation of thermodynamic properties [1, 2]<sup>1</sup>. As experimental specific heats  $C_v$  increase without limit on approach to the critical point [3, 4], this behavior is included in the present equation. The nonanalytic term is selected to conform with specific heats of parahydrogen at temperatures relatively far removed from the critical point. The general form of this isochoric equation of state can be related to the well-known Beattie-Bridgeman equation.

Three particular benefits derive from the present selection of temperature-dependent terms in the equation. Coefficients of these terms (found independently on each isochore of  $PVT$  data) are smooth functions of the density. Given the critical temperature, the present equation yields a critical density (and pressure) from  $PVT$  data in agreement with the known critical density of parahydrogen. Specific heats from the present equation agree with experimental data along near-critical isochores, without the use of complicated adjustments to the equation for the critical region. One may hope that present methods can be applied to other substances.

Data used in this work are from [5, 6]. Excellent reviews on critical phenomena are available [7, 8].

## 2. The Behavior of Specific Heats

Specific heats are related to  $(\partial^2 P/\partial T^2)_\rho$  from the equation of state by integration along isotherms:

\*This work was conducted at the National Bureau of Standards under the sponsorship of the U.S. Air Force (MIPR No. 4355-9-7).

\*\*Cryogenics Division, NBS Boulder Laboratories, Boulder, Colorado 80302.

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

$$C_v^* = -T \cdot \int_0^\rho (\partial^2 P / \partial T^2) d\rho / \rho^2 \quad (1)$$

where

$$C_v^* \equiv C_v(\rho, T) - C_v^0(T)$$

is the interaction specific heat, and  $C_v^0(T)$  at  $\rho=0$  refers to ideal gas states (translational and intramolecular effects only).

With any equation of state, eq (1) generally will yield several temperature-dependent terms for  $C_v^*$ . As  $T \rightarrow T_c$  along the critical isochore, however, there may be a nonanalytic term which exceeds all others. This term may be algebraic  $(T - T_c)^{-\alpha}$ , [9], or it may be logarithmic,  $-\log(T - T_c)$ , [10]. Assuming the algebraic form, we examine some parahydrogen data in figure 1 at  $\rho/\rho_c = 1.05$ . The slope of this log-log plot corresponds to exponent  $\alpha$ . For these data at  $T > 1.03 \cdot T_c$  the exponent  $\alpha = 3/4$  is not comparable with  $\alpha = 0.05$  deduced for other substances at  $T < 1.03 \cdot T_c$  [11]. We have used the argument  $\omega$  in figure 1 because integration will yield a power of  $T$  not exceeding unity in the equation of state. As background for figure 1, our oxygen specific heats were represented by use of  $\alpha = 1/3$  together with other terms [12].

### 3. An Origin for Temperature on Isochores

Consider the expression

$$C_v^* \sim [(T - T_c)/T]^{-\alpha}$$

at densities departing from the critical isochore D—C of figure 2. We must replace  $T_c$  by a locus of temperatures  $\theta(\rho)$  inside the coexistence envelope [12] which may serve as the origin for temperature along each isochore. If now we define the useful function of temperature along each isochore,

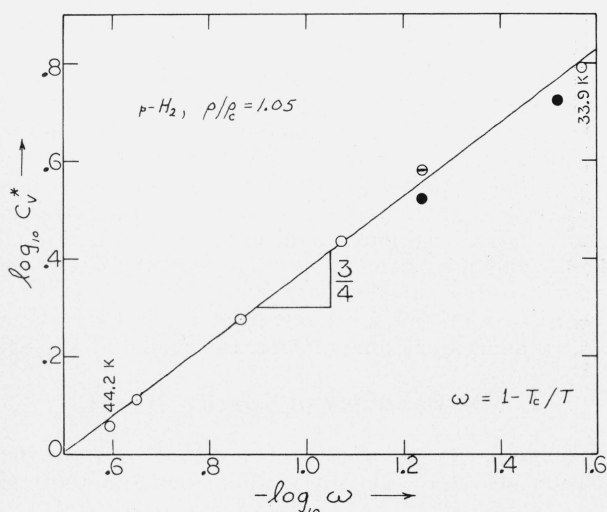


FIGURE 1. Interaction specific heats  $C_v^*$  (J/mol K) for p-H<sub>2</sub>. Open circles from [6]; filled circles from [2]; barred circle from [15].

$$\omega(\rho, T) \equiv 1 - \theta(\rho)/T, \quad (2)$$

we have in  $(1/\omega)$  a pole at the critical point approached from the one-phase domain.

To build an equation of state we need a formula for  $\theta(\rho)$ . An absolute description is difficult to formulate under the condition  $\theta \leq T_s$ . For present work, therefore, I define  $\theta$  as a fraction of the saturation temperatures formulated in the appendix. The following is selected from several definitions investigated:

$$\theta(\rho) = T_s(\rho) \cdot \exp[-a \cdot (\sigma - 1)^2]. \quad (3)$$

As the calculated  $T_s(\rho)$  terminates at the liquid triple point, we must for the present eliminate  $PVT$  data at higher densities. Equation (3) is arbitrary, but it permits us to go ahead with the formulation of an equation of state. It obviously deserves further investigation. It is interesting to note that the van der Waals' school uses a similar locus defined by maxima and minima of calculated isotherms inside the saturation envelope [14].

### 4. Formulation of the Nonanalytic Term

Consider the calculation of specific heats by means of (1) along the critical isotherm A—C—B of figure 2. As  $C_v$  is at a maximum at point C, it is necessary that  $\partial^2 P / \partial T^2$  change sign as density increases through the critical point. Assuming that one term alone in the equation of state is significant near point C, the change of sign may be given by a coefficient,  $D(\rho)$ , in the abbreviated equation:

$$P \sim D(\rho) \cdot \psi(\rho, T)$$

where  $\partial^2 \psi / \partial T^2 \rightarrow \infty$  as  $T \rightarrow \theta^+$ .

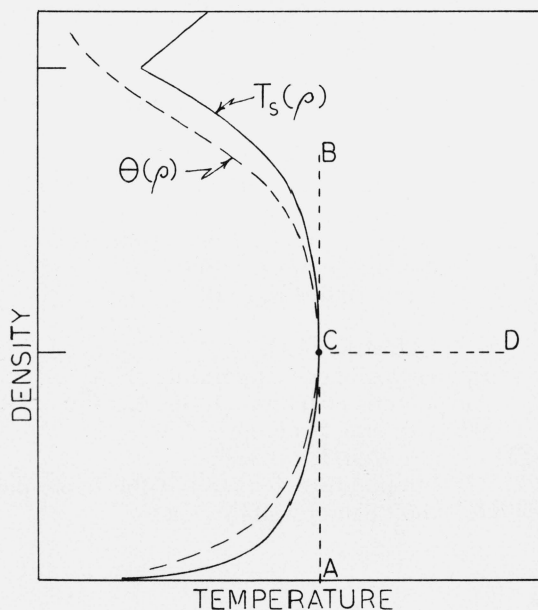


FIGURE 2. Density-temperature phase diagram.  $T_s(\rho)$  is the liquid-vapor coexistence envelope. Point C is the critical point.

Consider next that *PVT* isochores at  $\rho < \rho_c$  have only negative curvature, whereas at  $\rho > \rho_c$  they have positive curvature at low temperature, changing to negative curvature at high temperature [15]. To facilitate the construction of a wide-range equation of state, let the nonanalytic function have the same qualitative behavior as low-density isochores, figure 3.

Nonanalytic forms with monotonically negative curvature include:

$$\psi(\rho, T) \equiv \omega - \omega \cdot \log \omega, \quad (4a)$$

$$\psi(\rho, T) \equiv [\omega - \omega^{2-\alpha}/(2-\alpha)]/[1 - 1/(2-\alpha)], \quad (4b)$$

$$\psi(\rho, T) \equiv \omega + \delta \cdot \omega^2 \cdot \log \omega, \quad \delta \equiv \text{const.} \quad (4c)$$

All of these forms when used in (5) below give equally good representation of *PVT* data provided we omit the first point of every isochore (within 1 K of saturation). With (4c), pressures on the near-critical isotherm at 33 K cannot be represented acceptably. Function (4b) gives improving representation of *PVT* data as  $\alpha \rightarrow 1$ , leading to the selection of function (4a) for the equation of state.

### 5. The Equation of State

Our method is to postulate temperature-dependent terms in the equation of state. Coefficients of these terms are found by least squares independently on each isochore of *PVT* data. If, in addition to an accurate representation of the data, we obtain coefficients which are regular (smooth) functions of density, we may hope to develop the extremely precise descriptions required for these coefficients.

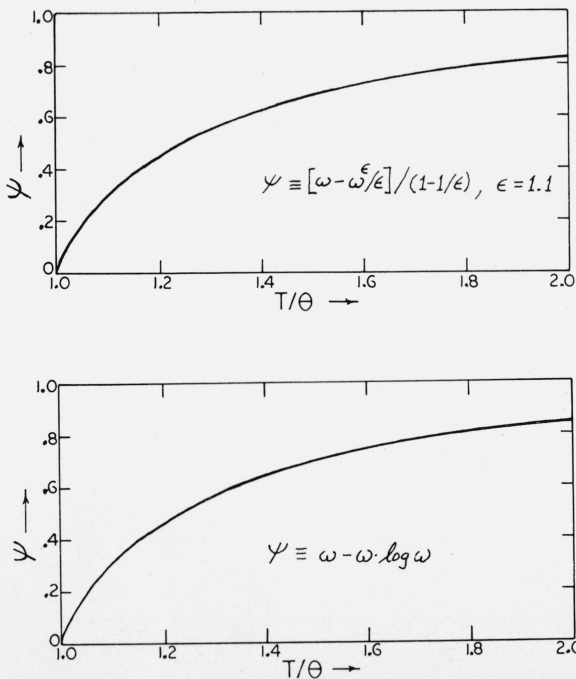


FIGURE 3. Two different functions  $\psi(\rho, T)$ , nonanalytic at  $T = \theta$ .

Equation of state (5) evolves from many exploratory computations with the interpolated *PVT* data on isochores [5]. Symbols are listed elsewhere. This equation uses  $\omega(\rho, T)$  defined by (2),  $\theta(\rho)$  defined by (3), and density-dependent coefficients  $A, B, C, D$ :

$$(Z-1) \cdot x/\rho = A + B \cdot \Phi(T) + C \cdot X(\rho, T) + D \cdot \Psi(\rho, T). \quad (5)$$

The temperature-dependent functions in (5) are

$$\Phi(T) \equiv x \cdot [1 - b \cdot \exp(-\beta/x)], \quad (5b)$$

$$X(\rho, T) \equiv \theta(\rho)/T, \quad (5c)$$

$$\Psi(\rho, T) \equiv 1 - [\omega - \omega \cdot \log \omega]. \quad (5d)$$

Function  $\Phi(T)$  is designed for freedom in high-temperature description of the second virial coefficient and to give at the same time a sensible behavior as  $T \rightarrow 0$ . The condensation of two terms into one is necessary to minimize the total number of terms in (5).

Function  $X(\rho, T)$  was selected by trial both for simplicity in  $C(\rho)$  and for representation of *PVT* data. As we shall have  $D(\rho) = 0$  on the critical isochore, it follows that the inflection on this isochore for parahydrogen is given by  $\Phi(T)$  and  $X(\rho, T)$  acting in concert. Efforts to condense this behavior into a single term have failed.

Function  $\Psi(\rho, T)$  gives the nonanalytic behavior  $\partial^2 \Psi / \partial T^2 \rightarrow \infty$  as  $T \rightarrow \theta$ , i.e. as  $\omega \rightarrow 0$ . Through definition (5d) this function approaches zero at high temperature. Its formulation was discussed above. At  $T \gg \theta$  we have  $\Psi \rightarrow (\theta/T)^2$ .

Density-dependent coefficients of (5) at first are obtained by least squares independently on each isochore of *PVT* data. Extreme precision is required in the representations of these coefficients because (5) gives a small difference of large values. For this reason we proceed in steps as follows:

(1) The original data for  $B(\rho)$  are seen in figure 4b. We select a linear form; transpose the calculated term  $B(\rho) \cdot \Phi(T)$  to the left side of (5); and redetermine  $A(\rho), C(\rho), D(\rho)$  on each isochore. Figure 4a gives these data for  $A(\rho)$ .

(2) A third order power series is selected for  $A(\rho)$  after testing in combination with other variables in (5). With the calculated  $A(\rho) + B(\rho) \cdot \Phi(T)$  on the left of (5) we redetermine data for  $C(\rho)$  and  $D(\rho)$ .

(3) We attack  $D(\rho)$  next due to our special interest in the root near  $\rho_c$ . The data of figure 4d suggest a cubic, but a fifth order series is necessary to reproduce *PVT* data. With three calculated terms transposed to the left of (5) we average  $C(\rho)$  on each isochore, with results in figure 4c.

For  $C(\rho)$  a seventh order series is found necessary by trial. All of these results are summarized as follows:

$$A(\rho) = \sum_{i=0}^3 A_i \cdot \rho^i, \quad C(\rho) = \sum_{i=0}^7 C_i \cdot \rho^i,$$

$$B(\rho) = \sum_{i=0}^1 B_i \cdot \rho^i, \quad D(\rho) = \sum_{i=0}^5 D_i \cdot \rho^i.$$

## 6. Discussion of Results

Interpolated data on 40 isochores are used at densities through 37.0 mol/l. The first point of each is omitted, leaving 953 *PVT* points for least squares determination of coefficients [5].

The hidden constants  $a$ ,  $b$ ,  $\beta$  in (5) may be investigated at various stages in formulating (5). Table 1 gives a survey using the above power series for coefficients  $A$ ,  $B$ ,  $C$ ,  $D$ . For each value of  $a$ ,  $b$ , and  $\beta$  we observe the mean relative deviation of 953 pressures in parts per ten thousand "*PCT*\* 100" and also the root in  $D(\rho)$ , "*D, ROOT*" in mol/l. For values  $a=0.2$ ,  $b=0.39$ ,  $\beta=10$ , the deviation is at a minimum 0.0203 percent and the root at 15.54 mol/l is in excellent agreement with  $15.27 \pm 0.30$  mol/l from [16] and with  $15.59 \pm 0.05$  from [2].

Table 2 gives all of the constants for equation of state [5]. At this critical point, 32.93 K and 15.54 mol/l, we obtain the following comparison with our vapor pressure equation [17]

	$P$ , atm	$P$ , MN/m <sup>2</sup>	$\frac{d \log P/d}{\log T}$
Equation (5)	12.628	1.2795	4.960
V.P. eq. [17]	12.673	1.2841	4.833

Table 3 gives calculated pressures (relative to the critical pressure) along the critical isotherm at 32.93 K. The small imperfection of this isotherm could arise for many reasons, including the need for a smaller critical exponent  $\alpha$  at temperatures very near  $T_c$ .

The most exacting check on (5), however, is the comparison of specific heats. We have selected data along near-critical isochores for this purpose. In tables 4 and 5 the data of Younglove and Diller are diminished to  $C_v^*$ . Density along the isochores is given on the first row. Columns from left to right give  $T$  and  $C_v^0$ ; then  $C_v^*$  from [6] and as calculated with (5); and last the difference of these values.

The authors ascribe an uncertainty of "several percent" at temperatures near saturation. The greatest difference, 0.46 J/mol K at 36.035 K in table 5, is 3.0 percent of the experimental  $C_v$ . It is interesting to make similar comparison with calculated specific heats from our monograph [2] in table 6 to see the increasing deviations as  $T \rightarrow T_c$ . Tedious and costly adjustments were required in [2] to conform with experimental  $C_v$  data, whereas (5) now gives acceptable values directly.

The Beattie-Bridgeman equation [18] may be written in the abbreviated, isochoric form

$$(Z-1) \cdot x/\rho = \bar{A}(\rho) + \bar{B}(\rho) \cdot x + \bar{D}(\rho)/x^2. \quad (7)$$

We note absence from (7) of a term in  $1/x$  like  $X(\rho, T)$  in (5). This might be related to the fact that  $C(\rho)$  in (5) is the only coefficient with origin near zero, figure 4c.

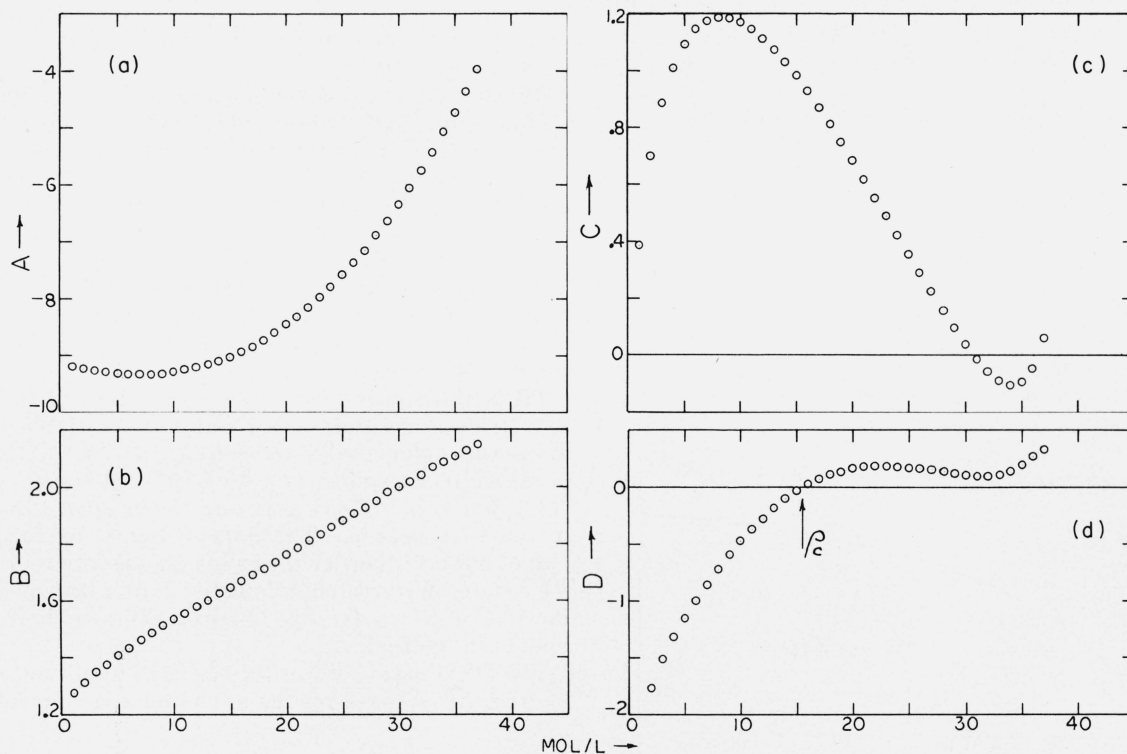


FIGURE 4. Density dependence of coefficients  $A$ ,  $B$ ,  $C$ ,  $D$ .

TABLE 1. Survey for constants a, b, and  $\beta$

		$a = 0.10$			
$\beta$	$b =$	0.38	0.39	0.40	0.41
8.00	PCT* 100 =	3.46	3.62	3.94	4.36
8.00	D, ROOT =	14.41	14.61	14.87	15.12
9.00	PCT* 100 =	2.62	2.88	3.29	3.81
9.00	D, ROOT =	14.90	15.14	15.40	15.68
10.00	PCT* 100 =	2.16	2.33	2.69	3.21
10.00	D, ROOT =	15.18	15.44	15.70	15.98
11.00	PCT* 100 =	2.57	2.39	2.56	2.88
11.00	D, ROOT =	15.28	15.53	15.79	16.06
		$a = 0.20$			
$\beta$	$b =$	0.38	0.39	0.40	0.41
8.00	PCT* 100 =	3.32	3.62	4.17	4.85
8.00	D, ROOT =	14.52	14.73	14.96	15.20
9.00	PCT* 100 =	2.31	2.63	3.22	3.95
9.00	D, ROOT =	15.01	15.25	15.50	15.77
10.00	PCT* 100 =	2.25	2.03	2.32	2.88
10.00	D, ROOT =	15.30	15.54	15.80	16.08
11.00	PCT* 100 =	3.51	3.01	2.67	2.71
11.00	D, ROOT =	15.41	15.64	15.89	16.16
		$a = 0.30$			
$\beta$	$b =$	0.38	0.39	0.40	0.41
8.00	PCT* 100 =	3.56	4.09	4.95	6.04
8.00	D, ROOT =	14.61	14.80	15.01	15.24
9.00	PCT* 100 =	2.50	2.70	3.57	4.65
9.00	D, ROOT =	15.11	15.33	15.57	15.84
10.00	PCT* 100 =	3.17	2.35	2.27	2.88
10.00	D, ROOT =	15.41	15.64	15.89	16.17
11.00	PCT* 100 =	5.27	4.45	3.72	3.16
11.00	D, ROOT =	15.54	15.76	15.99	16.26

TABLE 2. Constants of eq (5) for parahydrogen

$a = 0.2,$		$b = 0.39$	$\beta = 10$
$A_0 =$	-9.1083	1777	$C_4 =$ -488.5219 0867
$A_1 =$	-2.3668	5605	$C_5 =$ 606.6850 4566
$A_2 =$	5.5797	7042	$C_6 =$ -416.4729 0930
$A_3 =$	2.4230	4292	$C_7 =$ 120.7198 4869
$B_0 =$	1.2931	9156	$D_0 =$ -2.0898 5994
$B_1 =$	0.8959	3072	$D_1 =$ 8.0374 2211
$C_0 =$	0.1377	8548	$D_2 =$ -7.2966 5749
$C_1 =$	14.4323	0065	$D_3 =$ 1.9772 8697
$C_2 =$	-79.1011	8291	$D_4 =$ -6.3883 7912
$C_3 =$	242.3988	7393	$D_5 =$ 6.2341 2613

TABLE 3. Calculated critical isotherm

$d, \text{ mol/l}$	$P/P_c$
5.0	0.7373
6.0	.8165
7.0	.8779
8.0	.9237
9.0	.9564
10.0	.9785
11.0	.9918
12.0	.9991
13.0	1.0020
14.0	1.0021
14.5	1.0015
15.0	1.0008
15.5	1.0001
16.0	0.9994
16.5	.9989
17.0	.9987
18.0	.9995
19.0	1.0040
20.0	1.0149
21.0	1.0367
22.0	1.0748
23.0	1.1367
24.0	1.2309
25.0	1.3676
26.0	1.5584

TABLE 4. Comparison of  $C_v^*$  from [6] with calculated values from (5)

$T, \text{ K}$	$C_v^*$	$C_v^*$ at 13.28 mol/l		
		Publ	Calc	Diff
34.216	12.47	5.20	5.30	-0.10
36.402	12.48	2.79	3.09	-.30
38.384	12.48	2.08	2.21	-.13
40.214	12.49	1.66	1.75	-.07
42.107	12.51	1.41	1.41	-.00
43.985	12.52	1.25	1.20	.05
45.940	12.55	1.13	1.06	.07
47.994	12.59	1.02	0.95	.07
50.057	12.63	0.97	.88	.09
59.868	13.08	.80	.75	.05
69.974	13.98	.70	.72	-.02
80.206	15.34	.69	.70	-.01
90.055	16.94	.63	.68	-.05

Note:  $C_v^*$  in J/mol K.



TABLE 5. Comparison of  $C_v^*$  from [6] with calculated values from (5)

T, K	$C_v^*$	$C_v^*$ at 16.18 mol/l		
		Publ	Calc	Diff
33.889	12.47	6.17	6.07	0.10
36.035	12.48	2.73	3.19	-.46
38.194	12.48	1.90	2.13	-.23
42.244	12.51	1.30	1.30	.00
44.245	12.53	1.16	1.11	.05
46.166	12.55	1.08	0.99	.09
49.986	12.63	0.98	.87	.11
59.894	13.08	.84	.81	.03
69.931	13.98	.85	.83	.02
80.052	15.31	.79	.83	-.04
89.943	16.94	.76	.81	-.05

Note:  $C_v^*$  in J/mol K.

TABLE 6. Comparison of  $C_v^*$  from [2] with calculated values from (5)

T, K	$C_v^*$	$C_v^*$ at 15.50 mol/l		
		Publ	Calc	Diff
33.000	12.47	7.24	13.09	-5.85
34.000	12.47	5.44	5.91	-0.47
35.000	12.48	3.69	4.23	-.54
36.000	12.48	2.89	3.30	-.41
37.000	12.48	2.16	2.69	-.53
38.000	12.48	2.08	2.26	-.18
39.000	12.49	1.84	1.94	-.09
40.000	12.49	1.65	1.70	-.05
42.000	12.51	1.37	1.36	.01
44.000	12.52	1.20	1.15	.04
46.000	12.55	1.08	1.02	.06
48.000	12.59	1.00	0.93	.07
50.000	12.63	0.96	.88	.08
55.000	12.81	.91	.81	.10
60.000	13.08	.84	.80	.04
65.000	13.47	.80	.80	-.00
70.000	13.98	.77	.80	-.03
75.000	14.59	.77	.80	-.04
80.000	15.31	.76	.80	-.04
85.000	16.10	.77	.79	-.02
90.000	16.94	.79	.78	.01
95.000	17.82	.81	.77	.05
100.000	18.69	.84	.75	.09

Note:  $C_v^*$  in J/mol K.

The term  $1/x^2$  in (7) is qualitatively similar to  $\Psi(\rho, T)$  at  $T > \theta$ . Equation (7), however, suffers from coefficient  $\bar{D}(\rho)$  which is negative at all densities [18].

The virial equation [18] probably can be related to (5) only at such high temperatures that the last two terms of (5) are negligible. Figure 2 suggests that  $\theta(\rho)$  may not be analytic at  $\rho = 0$ .

### 7. Appendix. Temperature-density Formula for Coexisting Liquid and Vapor

This relation from [13] is in reduced variables,  $\tau \equiv T/T_c$ , and  $\sigma \equiv d/d_c$ ,

$$e^{a_0 \cdot (1-1/\tau)} = 1 - (\sigma - 1)^{8/3} \cdot e^{-\sigma \cdot f(\sigma)},$$

where

$$f(\sigma) \equiv a_1 + a_2 \cdot \sigma^{-1/3} + a_3 \cdot \sigma^{1/3} + a_4 \cdot \sigma^{8/3} + a_5 \cdot \sigma^3 + a_6 \cdot \sigma^7.$$

Values for the constants are,

$$\begin{aligned} a_0 &= 2.97647 & a_4 &= 0.620 & 5095 \\ a_1 &= 2.030 & 0583 & a_5 &= -0.421 & 81139 \\ a_2 &= -0.058 & 7951 & a_6 &= 0.682 & 5745 \cdot 10^{-3} \\ a_3 &= -1.856 & 5706 & & & \end{aligned}$$

The temperature-density relation for coexisting liquid and vapor is central to the present equation of state. Simplification and increase of accuracy in the description of this relation therefore is valuable, as obtained with the following form using symbols defined above,

$$(1/\tau - 1) = |\sigma - 1|^3 \cdot F(\rho),$$

$$F(\rho) \equiv a_1 \cdot \log_e(1/\rho) + a_2 + a_3 \cdot \rho + \dots + a_9 \cdot \rho^7.$$

Constants used and found for this expression are:

$$T_c = 32.953 \text{ K}, d_c = 15.59 \text{ mol/l},$$

$$\begin{aligned} a_1 &= 0.300 & 6242 & a_6 &= -237.846 & 2970 \\ a_2 &= -0.567 & 0332 & a_7 &= 331.544 & 2639 \\ a_3 &= 3.838 & 7436 & a_8 &= -231.236 & 7070 \\ a_4 &= -19.378 & 2878 & a_9 &= 64.190 & 7466 \\ a_5 &= 89.909 & 2005 & & & \end{aligned}$$

Maximum relative deviations for  $\tau$  are 0.03 percent as compared with 0.52 percent in [13]. The overall rms relative deviation is 0.016 percent as compared with a mean relative deviation of 0.062 percent in [13].

### 8. References

- [1] Landis, F., and Nilson, E. N., The determination of thermodynamic properties by direct differentiation techniques, sec. 21 in Progress in International Research on Thermodynamic and Transport Properties, J. F. Masi and D. H. Tsai, editors (Academic Press, New York, 1962).
- [2] Roder, H. M., Weber, L. A., and Goodwin, R. D., Thermodynamic and related properties of parahydrogen from the triple point to 100 K at pressures to 340 atmospheres, NBS Monograph 94 (Aug. 1965).
- [3] Michels, A., and Strijland, J., The specific heat at constant volume of compressed carbon dioxide, Physica **18**, Nos. 8-9, 613-628 (1952).
- [4] Voronel', A. V., and Chashkin, Yu. R., Measurement of the isochoric thermal capacity near the critical liquid-vapor point, Meas. Tech. (USSR) No. 11, 1387-1394 (Nov. 1967).
- [5] Goodwin, R. D., Diller, D. E., Roder, H. M., and Weber, L. A., Pressure-density-temperature relations of fluid parahydrogen from 15 to 100 K at pressures to 350 atmospheres, J. Res. NBS **67A**, Phys. and Chem., No. 2, 173-192 (1963).
- [6] Younglove, B. A., and Diller, D. E., The specific heat at constant volume of parahydrogen at temperatures from 15 to 90 K and pressures to 340 atm, Cryogenics **2**, No. 6, 348-352 (Dec. 1962).
- [7] Green, M. S., and Sengers, J. V., Editors, Critical Phenomena, NBS Miscellaneous Publication 273 (1966).

- [8] Sengers, J. V., and Sengers, A. L., The critical region, *Chem. & Eng. News* **46**, 104-118 (June 10, 1968).
- [9] Fisher, M. E., Correlation functions and the critical region of simple liquids, *J. Math. Phys.* **5**, No. 7, 944-961 (1964).
- [10] Yang, C. N., and Yang, C. P., Critical point in liquid-gas transitions, *Phys. Rev. Letters* **13**, No. 9, 303-305 (1964).
- [11] Vicentini-Missoni, M., and Levelt Sengers, J. M. H., Thermodynamic anomalies of CO<sub>2</sub>, Xe, & He<sup>4</sup> in the critical region, *Phys. Rev. Letters* **22**, No. 9, 389-393 (March 1969).
- [12] Goodwin, R. D., and Weber, L. A., Specific heats  $C_p$  of fluid oxygen from the triple point to 300 K at pressures to 350 atmospheres, *J. Res. NBS* **73A**, Phys. and Chem., No. 1, 15-24 (1969).
- [13] Goodwin, R. D., Density-temperature formulae for coexisting liquid and vapor and for freezing liquid parahydrogen, *J. Res. NBS* **70A**, Phys. and Chem., No. 6, 541-544 (1966).
- [14] See for example, Prigogine, I., and Defay, R., *Chemical Thermodynamics*, (Longmans Green & Co., London, 1954). This was pointed out by M. J. Hiza at NBS, Boulder, Colo.
- [15] Goodwin, R. D., An equation of state for fluid parahydrogen from the triple point to 100 K at pressures to 350 atmospheres, *J. Res. NBS* **71A**, Phys. and Chem., No. 3, 203-212 (1967).
- [16] Hoge, H. J., and Lassiter, J. W., Critical temperatures, pressures, and volumes of hydrogen, deuterium, and hydrogen deuteride, *J. Res. NBS* **47**, No. 2, 75-79 (1951) RP 2229.
- [17] Weber, L. A., Diller, D. E., Roder, H. M., and Goodwin, R. D., The vapor pressure of 20 K equilibrium hydrogen, *Cryogenics* **2**, No. 4, 236-238 (June 1962).
- [18] See for example, Dodge, Barnett F., *Chemical Engineering Thermodynamics*, first edition, p. 183-185 (McGraw-Hill Book Co., 1944).
- [19] Woolley, H. W., Scott, R. B., and Brickwedde, F. G., Compilation of thermal properties of hydrogen in its various isotopic and ortho-para modifications, *J. Res. NBS* **41**, No. 5, 379-475 (1948) RP 1932.

(Paper 73A6-571)