International Journal of Thermophysics, Vol. 16, No. 1, 1995

Equations of State for the Thermodynamic Properties of R32 (Difluoromethane) and R125 (Pentafluoroethane)[1]

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Thermodynamic properties of difluoromethane (R32) and pentafluoroethane (R125) are expressed in terms of 32-term modified Benedict-Webb-Rubin (MBWR) equations of state. For each refrigerant, coefficients are reported for the MBWR equation and for ancillary equations used to fit the ideal-gas heat capacity and the coexisting densities and pressure along the saturation boundary. The MBWR coefficients were determined with a multiproperty fit that used the following types of experimental data: PVT; isochoric, isobaric, and saturated-liquid heat capacities; second virial coefficients; and properties at coexistence. The respective equations of state accurately represent experimental data from 160 to 393 K and pressures to 35 MPa for R32 and from 174 to 448 K and pressures to 68 MPa for R125 with the exception of the critical regions. Both equations give reasonable results upon extrapolation to 500 K and 60 MPa. Comparisons between predicted and experimental values are presented.

KEY WORDS: difluoromethane (R32); equation of state; pentafluoroethane (R125); thermodynamic properties.

1. INTRODUCTION

R32 and R125 show promise (especially as components of mixtures) as replacements for R22 for use in small air-conditioning systems and heat pumps. In this work, available experimental data have been used to determine coefficients for two 32-term modified Benedict–Webb–Rubin (MBWR) equations of state, one for pure R32 and one for pure R125. Results are presented comparing predicted values to experimental data.

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[1] Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19–24, 1994, Boulder, Colorado, U.S.A.

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Table I. Summary of Experimental Data Used in the Correlation for R32

Investigator(s)	Ref. No.	Data type	Number of data points used	Temperature range (K)	Pressure range (MPa)
Defibaugh et al.	1	PVT (densimeter)	210	243–373	2.0–6.5
		PVT (Burnett)	149	268–373	0.03–0.98
		P_σ	18	268–348	0.7–5.4
		ρ_V	24	220–351	0.9–5.7
Holcomb et al.	2	P_σ	21	301–349	1.8–5.5
		ρ_L	22	301–349	1.8–5.5
Holste	3	PVT	103	150–375	1.5–72
Lüddecke and Magee	4	C_V	73	152–341	3.9–32
		C_σ	95	141–342	0.0001–4.8
Magee and Howley	5	PVT	146	140–393	3.8–35

2. DATA SOURCES

Tables I and II list the data that were used in the determination of the coefficients for the correlations of R32 and R125. In each case, the data sets used include both the liquid and the vapor phases and cover a large range in temperature and pressure. In Tables I and II the number of points listed for each data set was the number of points used in the final correlations and does not always represent the total number of points available; points

Table II. Summary of Experimental Data Used in the Correlation for R125

Investigator(s)	Ref. No.	Data type	Number of data points used	Temperature range (K)	Pressure range (MPa)
Boyes and Weber	6	PVT	84	293–363	0.3–4.5
Defibaugh and Morrison	7	PVT	90	273–369	1.5–6.3
		ρ_L	7	275–338	0.7–3.3
Gillis	8	B	9	240–400	
Holste	9	PVT	163	180–350	1.2–68
Lüddecke and Magee	4	C_V	96	196–341	3.7–33
		C_σ	85	175–277	0.006–0.78
Magee and Howley	5	PVT	87	174–398	1.5–35
		P_σ	34	175–335	0.003–3.3
Weber and Silva	10	P_σ	66	219–335	0.07–3.3
Wilson et al.	11	PVT	48	198–448	2–10
		C_p	10	216–333	0.1–3.4

which were inconsistent with other experimental points were omitted. The equations were based on the ITS-90 temperature scale; data that were measured on IPTS-68 were converted before fitting.

The list of data sources in Tables I and II is not exhaustive; additional data are available. The present data were selected because of their high accuracy and comprehensive coverage of large ranges of temperature and pressure. The omission of other data from the literature does not necessarily reflect upon the merit of those data.

3. ANCILLARY EQUATIONS

An accurate representation of the saturation boundary is very important for refrigeration applications. To facilitate this, vapor pressure and saturated-liquid and saturated-vapor densities are fitted to separate ancillary equations. These functions are then used to define the saturation boundary in the fitting of the equation of state; these functions are used only in the fitting process, and are not part of the final MBWR equation. The functional forms chosen for vapor pressure, P_σ, of R32 and R125 are shown in Eqs. (1a) and (1b), respectively.

$$\ln\left[\frac{P_\sigma}{P_c}\right]=\frac{\alpha_0\tau+\alpha_1\tau^{1.5}+\alpha_2\tau^2+\alpha_3\tau^4+\alpha_4\tau^{6.5}}{1-\tau} \tag{1a}$$

$$\ln\left[\frac{P_\sigma}{P_c}\right]=\frac{\alpha_0\tau+\alpha_1\tau^{1.5}+\alpha_2\tau^3+\alpha_3\tau^6}{1-\tau} \tag{1b}$$

Equations for saturated-liquid density, ρ_L, and saturated-vapor density, ρ_V, are

$$\rho_L=\rho_c[1+d_0\tau^\beta+d_1\tau^{2/3}+d_2\tau+d_3\tau^{4/3}+d_4\tau^2+d_5\tau^3] \tag{2}$$

$$\rho_V=\frac{P_\sigma}{RT}\left[\left[\left[1+\frac{f_0\tau^\beta+f_1\tau^{2\beta}+f_2\tau+f_3\tau^2+f_4\tau^4}{1+f_5\tau}\right]\right.\right.$$

$$\left.\left.\times\frac{P_\sigma(Z_c-1)}{P_cT_r^8}\right]+1\right]^{-1} \tag{3}$$

where $T_r=T/T_c$, $\tau=1-T/T_c$, $\beta=0.355$, $Z_c=P_c/(\rho_cRT_c)$. The heat capacity of the ideal-gas reference state is needed to calculate energy-related quantities, such as enthalpy, from the MBWR equation of state; it has been fit to a simple polynomial in reduced temperature:

$$\frac{C_p^0}{R}=c_0+c_1T_r+c_2T_r^2+c_3T_r^3 \tag{4}$$

Table III. Coefficients for Ancillary Eqs. (1)–(4)

	0	1	2	3	4	5	RMS (%)
R32							
α_i	−7.559554	+2.465252	−1.976887	−2.021284	−1.941251		0.023
d_i	+2.290243	−0.609785	+2.460849	−1.598883	+0.366530	+0.221591	0.046
f_i	−0.675455	−1.672852	+0.163588	+2.903511	−4.039126	−0.009176	0.267
c_i	+4.425953	−2.664260	+5.579473	−1.679632			0.051
Critical parameters: $T_c = 351.35$ K [12], $P_c = 5.795$ MPa, $\rho_c = 8.2078$ mol · L^{-1} [13]							
R125							
α_i	−7.435645	+1.341794	−3.367536	−1.697153			0.062
d_i	+1.887307	+1.281660	−1.682786	+1.348140	0.0	0.0	0.047
f_i	−0.698842	−2.745433	+2.288954	+0.416675	0.0	0.0	0.166
c_i	+3.111514	+10.982115	−1.843797	+0.019273			0.036
Critical parameters: $T_c = 339.33$ K [12], $P_c = 3.629$ MPa, $\rho_c = 4.75996$ mol · L^{-1} [11]							

The coefficients for the ancillary equations and deviations from experimental data are listed in Table III. The critical parameters used for R32 and R125 are also listed in Table III. The critical pressures were determined by extrapolating the experimental vapor pressures of Defibaugh et al. [1] for R32 and Weber and Silva [10] for R125 to the critical temperatures of Schmidt and Moldover [12]. To ensure symmetry of the liquid and vapor branches of the saturation boundary at the critical point, the leading coefficient of the saturated-vapor density equation, f_0, is derived from the $d_0\tau^\beta$ term of the saturated-liquid density equation.

The vapor pressure fits for both R32 and R125 include data derived from the saturated-heat capacity, C_σ, data of Lüddecke and Magee [4]. These were calculated using a variation on the method described by Weber [14].

The saturated-liquid density fits include data extrapolated from the isochoric PVT data of Magee and Howley [5]. Saturated-vapor densities were extrapolated from the vapor PVT data of Defibaugh et al. [1]. The saturated-vapor density fits for both fluids also included data that were generated by intersecting a virial surface with the vapor pressure equation.

4. FORMULATION OF THE THERMODYNAMIC SURFACE

The MBWR equation used was that proposed by Jacobsen and Stewart [15]. The equation is applicable over wide temperature and pressure ranges

Table IV. Temperature Dependence of the MBWR Coefficients

$a_1 = RT$

$a_2 = b_1 T + b_2 T^{0.5} + b_3 + b_4/T + b_5/T^2$

$a_3 = b_6 T + b_7 + b_8/T + b_9/T^2$

$a_4 = b_{10} T + b_{11} + b_{12}/T$

$a_5 = b_{13}$

$a_6 = b_{14}/T + b_{15}/T^2$

$a_7 = b_{16}/T$

$a_8 = b_{17}/T + b_{18}/T^2$

$a_9 = b_{19}/T^2$

$a_{10} = b_{20}/T^2 + b_{21}/T^3$

$a_{11} = b_{22}/T^2 + b_{23}/T^4$

$a_{12} = b_{24}/T^2 + b_{25}/T^3$

$a_{13} = b_{26}/T^2 + b_{27}/T^4$

$a_{14} = b_{28}/T^2 + b_{29}/T^3$

$a_{15} = b_{30}/T^2 + b_{31}/T^3 + b_{32}/T^4$

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for both the liquid and the vapor phases except near the critical point. The equation has the following functional form:

$$P = \sum_{i=1}^{9} a_i(T)\,\rho^i + \exp(-\delta^2) \sum_{i=10}^{15} a_i(T)\,\rho^{2i-17} \tag{5}$$

where $\delta = \rho/\rho_c$. Formulas for the $a_i(T)$ are listed in Table IV.

The final equation of state is determined through an iterative process. Weights are assigned to the data by two methods: (1) a propagation of uncertainty calculation as described by Hust and McCarty [16] and (2) manually with respect to data type (e.g., PVT or C_V), individual data sets, or temperature, pressure, or density regions. Beginning with an initial set of 32 coefficients and the saturation boundary as defined by the ancillary equations, the fitting program performs a linear least-squares fit [16, 17] and calculates a new set of coefficients to minimize the deviations between experimental values and those predicted by the MBWR equation. Weights may then be adjusted, the new coefficients used as starting coefficients, and the process repeated until an equation is determined that represents the best compromise among the various data sets and data types. It is important to note here that this procedure sometimes involves compromising an excellent fit of one data set or data type for a better overall fit of the entire thermodynamic surface.

5. RESULTS

The coefficients determined for the fits of R32 and R125 to the MBWR equation are given in Tables V and VI. The coefficients correspond to

Table V. Coefficients for the MBWR Equation of State for R32

b_1	−0.131 275 4052 E−03	b_2	+0.899 927 9349 E+00	b_3	−0.281 400 8052 E+02
b_4	+0.436 091 1828 E+04	b_5	−0.837 235 2800 E+06	b_6	−0.782 176 4090 E−06
b_7	−0.111 226 6068 E+01	b_8	+0.539 331 4319 E+03	b_9	+0.288 600 2769 E+06
b_{10}	−0.352 264 6093 E−04	b_{11}	+0.189 661 8301 E+00	b_{12}	−0.686 549 0040 E+02
b_{13}	−0.349 007 0642 E−02	b_{14}	−0.749 983 5595 E−01	b_{15}	−0.321 524 2831 E+02
b_{16}	+0.913 057 9219 E−02	b_{17}	−0.171 082 1818 E−03	b_{18}	+0.503 986 9843 E−01
b_{19}	−0.830 354 8678 E−03	b_{20}	−0.245 522 6767 E+06	b_{21}	−0.107 859 0560 E+08
b_{22}	−0.429 514 2796 E+04	b_{23}	+0.808 724 7296 E+08	b_{24}	−0.125 945 2300 E+02
b_{25}	−0.105 735 0098 E+04	b_{26}	−0.904 064 7453 E−01	b_{27}	−0.183 578 7330 E+04
b_{28}	−0.169 690 6125 E−03	b_{29}	+0.639 250 8206 E−01	b_{30}	−0.204 925 7674 E−06
b_{31}	−0.165 629 7009 E−03	b_{32}	−0.932 607 4934 E−02		

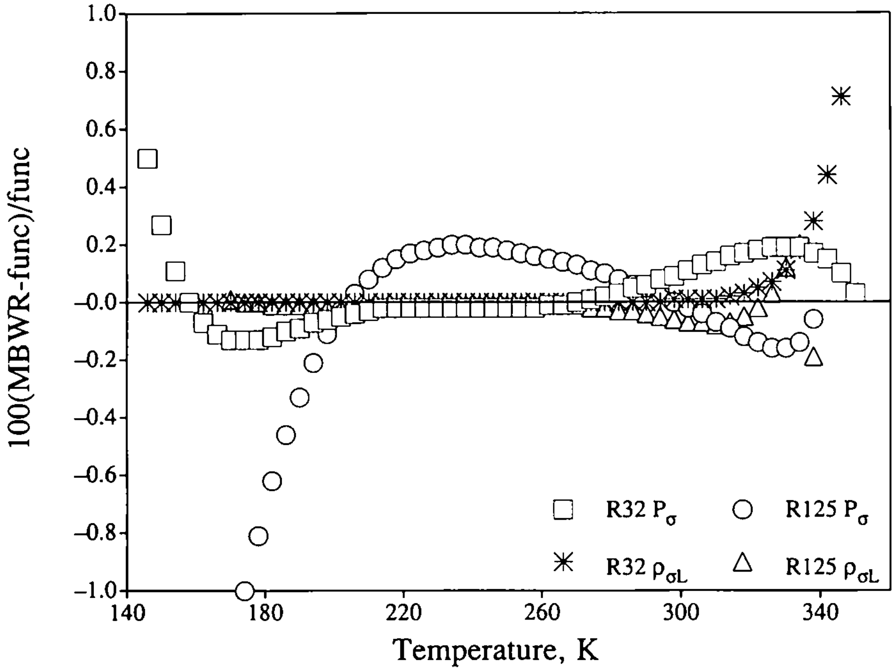

Fig. 1. Deviation of vapor pressures and saturated-liquid densities calculated by MBWR equations for R32 and R125 from ancillary equations.

Table VI. Coefficients for the MBWR Equation of State for R125

b_1	−0.523 369 6070 E−01	b_2	+0.378 761 8789 E+01	b_3	−0.807 152 8190 E+02
b_4	+0.115 654 6052 E+05	b_5	−0.152 175 6192 E+07	b_6	+0.597 541 4845 E−02
b_7	−0.145 990 5900 E+01	b_8	−0.992 338 9957 E+03	b_9	−0.399 180 5357 E+06
b_{10}	−0.722 591 0375 E−03	b_{11}	+0.358 108 0810 E+00	b_{12}	−0.108 627 9946 E+03
b_{13}	+0.229 821 6266 E−01	b_{14}	+0.149 537 6704 E+01	b_{15}	+0.911 199 8340 E+03
b_{16}	−0.254 479 9497 E+00	b_{17}	+0.102 433 8941 E−01	b_{18}	−0.645 583 1647 E+01
b_{19}	+0.218 649 9632 E+00	b_{20}	+0.114 748 7216 E+07	b_{21}	−0.118 389 8254 E+09
b_{22}	+0.306 539 7750 E+05	b_{23}	+0.542 870 2894 E+09	b_{24}	+0.903 502 6356 E+03
b_{25}	−0.153 646 5074 E+06	b_{26}	+0.314 617 9037 E+01	b_{27}	+0.429 297 5467 E+06
b_{28}	+0.109 652 0216 E+00	b_{29}	−0.329 350 2718 E+02	b_{30}	−0.338 796 9505 E−03
b_{31}	+0.384 533 6519 E+00	b_{32}	−0.491 511 7069E+02		

temperatures in K, pressures in bar, densities in mol/L, and a gas constant of $R = 0.083\ 144\ 71\ \text{L} \cdot \text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ [18].

Deviation plots of vapor pressure and saturated-liquid density, as calculated by the MBWR equation, are shown in Fig. 1. The baseline (or zero) represents the ancillary equations.

Figures 2 and 3 show R32 and R125 density deviations of experimental PVT data with values predicted by the MBWR equations of state as a

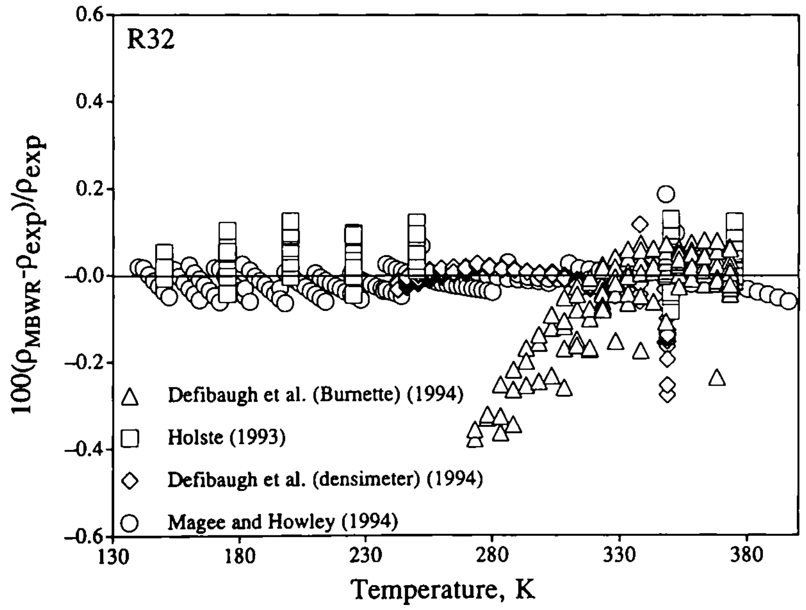

Fig. 2. Deviations of densities calculated by the MBWR fit for R32 from experimental densities.

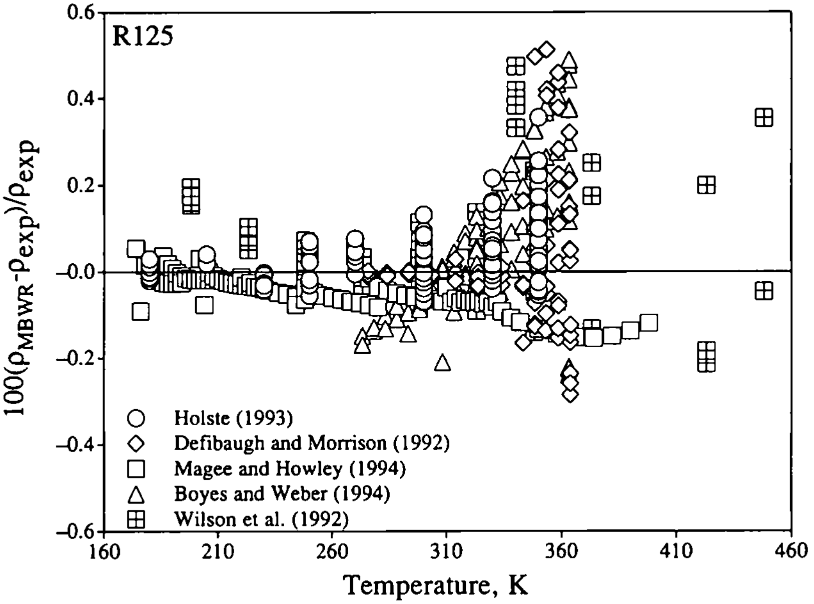

Fig. 3. Deviations of densities calculated by the MBWR fit for R125 from experimental densities.

Table VII. Average Absolute Deviation (AAD) and Bias of MBWR Correlations with Experimental PVT and Heat Capacity Data and the Ancillary Equations for the Saturation Boundary

	R32		R125	
Property	AAD (%)	Bias (%)	AAD (%)	Bias (%)
PVT				
Density deviation	0.041	−0.012	0.092	0.038
Pressure deviation	1.254	−0.361	1.403	−0.627
C_v	0.407	−0.167	0.438	−0.205
C_p			1.340	0.674
C_σ	1.112	−1.112	0.373	0.123
P_σ	0.072	0.033	0.206	−0.064
ρ_L	0.054	0.053	0.034	−0.017
ρ_V	0.997	−0.895	0.377	0.031

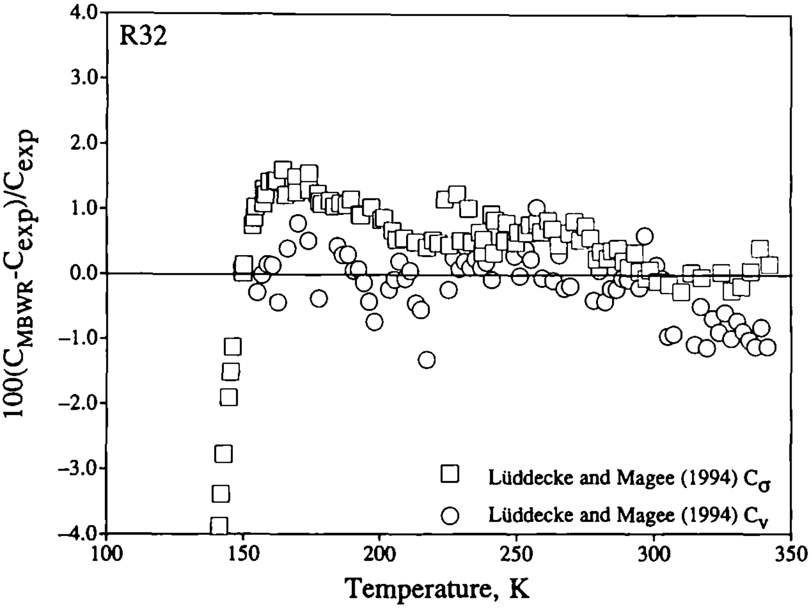

Fig. 4. Deviations of isochoric and two-phase heat capacities calculated by the MBWR fit of R32 from experimental values.

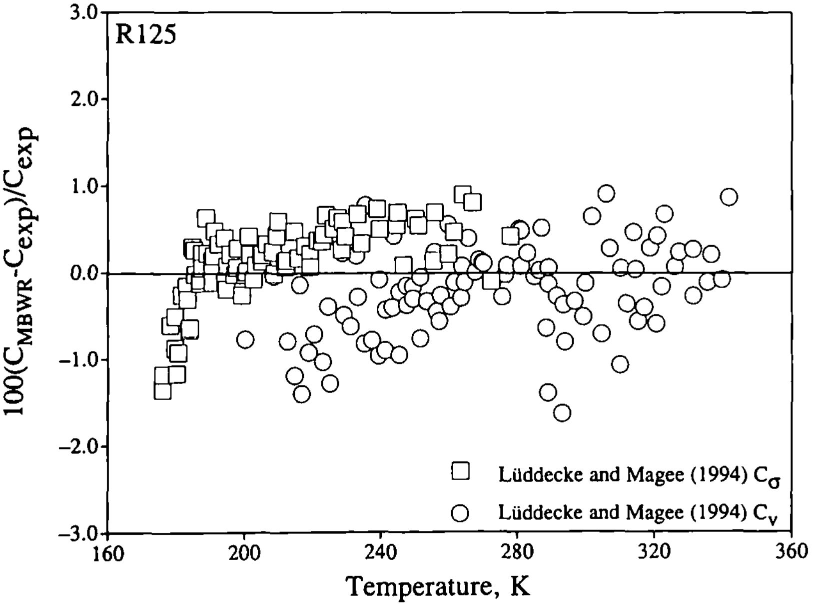

Fig. 5. Deviations of isochoric and two-phase heat capacities calculated by the MBWR fit of R125 from experimental values.

function of temperature. The R32 densities in the liquid phase agree within ±0.14% except near the critical point. The vapor densities of Defibaugh [1] are fitted to ±0.4%. Most of the R125 densities (Fig. 3) are fitted to ±0.2% with the exceptions of temperatures close to critical and the low-density, high-temperature data of Wilson et al. [11]. Overall statistical results are given in Table VII.

Deviation plots for C_V and C_σ for R32 and R125 are shown in Figs. 4 and 5. The plot for R32 shows that most of the points are within 1.5%, with a maximum deviation in C_σ of 3.9% near the triple point. For R125, the equation-of-state values show a maximum deviation of approximately 1.7% from the experimental values. As with R32, the deviations in R125 C_σ are largest near the triple point.

6. CONCLUSIONS

Equations of state based on multiproperty fits for R32 and R125 have been presented. The correlations were based on an MBWR equation. These equations of state represent, to a high accuracy, the thermodynamic properties over the full range of experimental data (with the exception of the critical region) and also give reasonable results upon extrapolation to 500 K and 60 MPa.

ACKNOWLEDGMENTS

We thank our colleagues whose data we used prior to publication: S. A. Boyes, D. R. Defibaugh, K. A. Gillis, J. C. Holste, J. B. Howley, T. O. D. Lüddecke, J. W. Magee, G. Morrison, J. W. Schmidt, and L. A. Weber. Support for this work was provided by the Air Conditioning and Refrigeration Technology Institute.

REFERENCES

1. D. R. Defibaugh, G. Morrison, and L. A. Weber, *J. Chem. Eng. Data* **39**:333 (1994).
2. C. D. Holcomb, V. G. Niesen, L. J. VanPoolen, and S. L. Outcalt, *Fluid Phase Equil.* **91**:145 (1993).
3. J. C. Holste, private communication, Texas A&M University (1993).
4. T. O. D. Lüddecke and J. W. Magee, private communication, NIST, Boulder, CO (1994).
5. J. W. Magee and J. B. Howley, private communication, NIST, Boulder, CO (1994).
6. S. A. Boyes and L. A. Weber, submitted for publication (1994).
7. D. R. Defibaugh and G. Morrison, *Fluid Phase Equil.* **80**:157 (1992).
8. K. A. Gillis, NIST, private communication, Gaithersburg, MD (1994).
9. J. C. Holste, Thermodynamic Properties of Refrigerants R-125 and R-141b; Final Report to ASHRAE on Project RP-654 (1993).

10. L. A. Weber and A. M. Silva, *J. Chem. Eng. Data* **39**:809 (1994).
11. L. C. Wilson, W. V. Wilding, G. M. Wilson, R. L. Rowley, V. M. Felix, and T. Chilsom-Carter, *Fluid Phase Equil.* **80**:167 (1992).
12. J. W. Schmidt and M. R. Moldover, *J. Chem. Eng. Data* **39**:39 (1994).
13. Y. Higashi, H. Imaizumi, and S. Usuba, *13th Jap. Symp. Thermophys. Prop.* (1992), p. 65.
14. L. A. Weber, *Int. Refrig. Conf.* West Lafayette, IN, July 14–17 (1992), p. 463.
15. R. T. Jacobsen and R. B. Stewart, *J. Phys. Chem. Ref. Data* **21**:757 (1973).
16. J. G. Hust and R. D. McCarty, *Cryogenics* **7**:200 (1967).
17. R. D. McCarty, in *Experimental Thermodynamics, Vol. II*, B. Le Neindre and B. Vodar, eds. (Butterworth, London, 1975), pp. 501–526.
18. M. R. Moldover, J. P. M. Trusler, T. J. Edwards, J. B. Mehl, and R. S. Davis, *J. Res. NBS* **93**:85 (1988).