International Journal of Thermophysics, Vol. 22, No. 6, November 2001 (© 2001)

A New Generalized Four-Parameter Corresponding-States Method for Predicting Volumetric Behavior of Working Fluids

W. L. Cheng,[1, 2] Z. S. Chen,[1] P. Hu,[1] and L. Jia[1]

Received October 27, 2000

A new four-parameter corresponding-states method is presented to correlate the generalized volumetric behavior of polar and nonpolar working fluids. It is different from other corresponding-states methods in that the acentric factor is not used, instead the normal boiling temperature and critical compressibility factor are introduced as basic parameters. Comparison between experimental and calculated volumetric properties shows that highly accurate results are obtained by the new method for 18 polar and nonpolar working fluids with 3900 experimental data. The overall average absolute error for all of the fluids studied is about 0.8%.

KEY WORDS: corresponding states; prediction method; refrigerants; thermodynamic properties.

1. INTRODUCTION

Ozone-depleting refrigerants, such as CFCs and HCFCs, are currently being phased out. The identification of alternative refrigerants is of essential importance, and this identification requires extensive data for thermodynamic properties. However, measurements of those data will cost substantial money and time. If a more accurate model is developed, the selection of new alternative refrigerants will be possible with minimal measurement of some fundamental properties. This study has focused on the corresponding-states principle for the prediction of the *PVT* properties of refrigerants.

---

[1] Department of Thermal Science and Energy Engineering, University of Science and Technology of China, Hefei, Anhui 230027, People's Republic of China.

[2] To whom correspondence should be addressed. E-mail: wlcheng@ustc.edu.cn

Chen et al. [1–3] have developed general corresponding-states formulas with a high accuracy to predict the saturation properties of working fluids. The corresponding-states principle is often applied to predict the thermodynamic properties in the entire fluid regions of refrigerants [4–9].

The original corresponding-states method can be expressed with the reduced parameters P_r, V_r, and T_r, which have a corresponding relationship for different substances. The compressibility factor Z can be described by a function of reduced pressure P_r and reduced temperature T_r:

$$Z = f(P_r, T_r) \tag{1}$$

The reduced pressure $P_r = P/P_c$, the reduced temperature $T_r = T/T_c$, the compressibility factor $Z = PV/RT$, R is the gas constant, and the subscript c indicates critical parameters. Of course, it is difficult to obtain a high accuracy with Eq. (1). Therefore, a new parameter, the acentric factor ω, was introduced by Pitzer [4], and a three-parameter corresponding-states method was obtained:

$$Z = f(P_r, T_r, \omega) \tag{2}$$

Since then, several modifications have been produced to correlate better the volumetric behavior of fluids. Lee and Kesler (LK model) successfully extended the three-parameter corresponding-states method [5]. The LK model can give an acceptable accuracy for nonpolar and slightly polar substances; however, for polar substances the prediction results of the LK correlation are not reasonable. Therefore, a four-parameter corresponding-states method was proposed by Wu and Stiel (WS model) [6]. Based on the LK model, a polar fluid correction term is appended in the WS model as the fourth parameter. Wilding and Rowley developed another four-parameter model (WR model) [7] and suggested that geometry and polarity effects might be separable. Scalabrin, Santo, and Grigiante (SSG) [8] modified the WR model. Having studied the four-parameter corresponding-states models, Park, Sonntag, and Borgnakke proposed a new model (PSB model) [9]. In this model, the acentric factor is retained as the third parameter, and a new parameter that is proportional to the logarithm of the compressibility factor of a saturated liquid at a reduced temperature of 0.7 is introduced as the fourth parameter. This model can give a much higher accuracy than the others.

In this study, the third and fourth parameters are replaced by the reduced normal boiling temperature T_{br} and the critical compressibility factor Z_c, respectively. Since T_{br} and Z_c are basic parameters for any fluid, and T_{br} is much easier to measure than the acentric factor, those two parameters are reasonable as the third and fourth parameters in a four-parameter corresponding-states model. Unlike other methods, the third and fourth parameters are not necessarily equal for nonpolar fluids. However, these two parameters are used to reflect the combined effects due to polarity and geometry.

2. A NEW FOUR-PARAMETER CORRESPONDING-STATES MODEL

In this study, P_r, T_r, κ, and λ are selected as the four parameters of the new four-parameter corresponding-states model. Thus, the compressibility factor is expressed as

$$Z = f(P_r, T_r, \kappa, \lambda) \tag{3}$$

where the third parameter κ and the fourth parameter λ are functions of the reduced normal boiling temperature T_{br} and the critical compressibility factor Z_c. They are assumed to have a linear relationship with T_{br} and Z_c, respectively,

$$\kappa = a - T_{br} \tag{4}$$

$$\lambda = b - Z_c \tag{5}$$

The reduced normal boiling temperature $T_{br} = T_b/T_c$, T_b is the normal boiling temperature, and the critical compressibility factor $Z_c = P_c V_c/(RT_c)$.

Equation (3) is expanded by the Taylor method and the second-order term is ignored:

$$Z = Z^{(0)} + \kappa Z^{(1)} + \lambda Z^{(2)} \tag{6}$$

In Eq. (6), $Z^{(0)}$, called the standard compressibility factor, is the compressibility factor when both κ and λ are zero. $Z^{(1)}$ and $Z^{(2)}$ are used to modify the difference between the compressibility factor of practical fluids and the standard compressibility factor. It can be assumed that $Z^{(0)}$, $Z^{(1)}$, and $Z^{(2)}$ are all functions of P_r and T_r for different fluids.

It should be noted that $Z^{(0)}$ is related to the values of coefficients a and b in Eqs. (4) and (5). A reference function for $Z^{(0)}$ can be defined either using the compressibility factor of a specific fluid or using the average of several kinds of fluids. It is noted that the reduced normal boiling temperature T_b is about 0.66 for most fluids. To keep the third parameter κ near zero, the coefficient a in Eq. (4) is assumed to be 0.66. Since the critical compressibility factors for nonpolar fluids (such as argon, krypton, xenon, and methane, etc.) are near 0.291, for the same reason, the coefficient b in

Eq. (5) is determined as 0.291. In fact, the values of a and b do not affect the prediction results very much. Then Eqs. (4) and (5) can be replaced by

$$\kappa = 0.66 - T_{\mathrm{br}} \tag{7}$$

$$\lambda = 0.291 - Z_{\mathrm{c}} \tag{8}$$

If we select three fluids as reference fluids, it is not necessary to determine the $Z^{(i)}$ ($i = 1, 2, 3$) of the fluid of interest. The compressibility factor of the fluid of interest can be calculated from the compressibility factors of the reference fluids. According to Eq. (6), the compressibility factor of each reference fluid can by expressed by the following equation:

$$Z_i = Z^{(0)} + \kappa_i Z^{(1)} + \lambda_i Z^{(2)} \qquad (i = 1, 2, 3) \tag{9}$$

At the same time, the compressibility factor of any fluid of interest can be expressed by a linear combination of these three reference fluids:

$$Z = \alpha Z_1 + \beta Z_2 + (1 - \alpha - \beta)\, Z_3 \tag{10}$$

In Eq. (10), the compressibility factors Z_1, Z_2, and Z_3 are the compressibility factors of these three reference fluids. Coefficients α and β are the weighting factors for the fluid of interest related to the three reference fluids. Combining with Eqs. (6), (9), and (10), a set of equations for α and β is obtained:

$$\alpha(\kappa_1 - \kappa_3) + \beta(\kappa_2 - \kappa_3) = \kappa - \kappa_3 \tag{11a}$$

$$\alpha(\lambda_1 - \lambda_3) + \beta(\lambda_2 - \lambda_3) = \lambda - \lambda_3 \tag{11b}$$

From Eqs. (11a) and (11b), expressions for α and β are obtained:

$$\alpha = [(\kappa - \kappa_3)(\lambda_2 - \lambda_3) - (\lambda - \lambda_3)(\kappa_2 - \kappa_3)]/\mathrm{DIV} \tag{12a}$$

$$\beta = [(\lambda - \lambda_3)(\kappa_1 - \kappa_3) - (\kappa - \kappa_3)(\lambda_1 - \lambda_3)]/\mathrm{DIV} \tag{12b}$$

$$\mathrm{DIV} = (\kappa_1 - \kappa_3)(\lambda_2 - \lambda_3) - (\kappa_2 - \kappa_3)(\lambda_1 - \lambda_3) \tag{12c}$$

In this work, the third parameter κ and the fourth parameter λ are not always zero for a nonpolar fluid, and this is different from other four-parameter corresponding-states equations. Their values can be different for different fluids. But κ and λ reflect the basic attributes of interest of fluids and are easily determined.

In this way, if the critical parameters and normal boiling point of a fluid of interest are known, the thermodynamic properties of the fluid of interest can be calculated using Eqs. (9) and (10).

3. REFERENCE FLUIDS

The four-parameter corresponding-states model is a cubic interpolation in substance. The values of the three reference fluids for the interpolation should have extensive representation. To generalize this method, the three reference substances should have relatively great differences in properties, and they should each represent a different class of fluids. On the other hand, the reference fluids should be chosen to be similar to the fluid of interest, to increase the calculation accuracy.

The accuracy of the reference substances' thermodynamic properties directly influences the calculation precision for the fluid of interest by the four-parameter corresponding-states model. Those substances with highly accurate thermodynamic properties should be selected as reference substances. In this work, water, propane, and oxygen were selected as reference substances.

The thermodynamic properties of water, propane, and oxygen can be directly obtained from the PROPATH database, which is provided by Kyushu University of Japan [10]. In the database, the state equations of water, propane, and oxygen come from Refs. 11, 12, and 13, respectively.

Table I. Basic Parameters of Working Fluids

Fluid	P_c (MPa)	T_c (K)	V_c ($10^{-3}\,m^3kg^{-1}$)	Z_c	T_b (K)	κ	λ	Data source (first author)
H_2O	22.12	647.30	3.1700	0.2347	373.15	0.08353	0.0563	JSME [11]
O_2	5.043	154.58	2.2925	0.2878	90.185	0.07658	0.0032	Sychev [13]
C_3H_8	4.260	369.90	4.5450	0.2776	231.51	0.03413	0.0134	Buehner [12]
R152a	4.517	386.41	2.7170	0.2523	249.13	0.01527	0.0387	Tillner-Roth [14]
i-C_4H_{10}	3.640	407.85	4.4560	0.2780	261.54	0.01873	0.0130	William [15]
R236fa	3.200	398.07	1.8139	0.2666	271.74	−0.0226	0.0244	Giovanni [16]
R124	3.624	395.43	1.7857	0.2686	261.19	−0.0005	0.0224	Boyes [17]
R23	4.836	299.07	1.9047	0.2593	191.05	0.02119	0.0317	Hou [19]
R22	4.990	369.30	1.9091	0.2683	232.34	0.03086	0.0227	JAR [41]
R123	3.662	456.83	1.8180	0.2680	300.97	0.00118	0.0230	Piao [22]
R14	3.750	227.51	1.5982	0.2788	145.11	0.02218	0.0122	Platzer [40]
R113	3.392	487.21	1.7857	0.2802	320.74	0.00168	0.0108	Martin [24]
R12	4.136	385.12	1.7699	0.2764	243.36	0.02809	0.0146	Prasad [25]
R500	4.426	378.70	2.0121	0.2808	239.73	0.02697	0.0102	Platzer [40]
R141b	4.250	477.35	2.1739	0.2722	305.20	0.02064	0.0188	Maezawa [27]
R142b	4.041	410.29	2.2422	0.2669	264.15	0.01619	0.0241	Maezawa [28]
R143a	3.764	345.86	2.3042	0.2537	225.93	0.00710	0.0373	Tillner-Roth [43]
R134a	4.059	374.18	1.9685	0.2609	247.08	−0.0005	0.0301	Tillner-Roth [43]
CH_4	4.595	190.56	6.1656	0.2869	111.63	0.07417	0.0041	Angus [42]
R245ca	3.925	447.57	1.9098	0.2700	298.28	−0.0064	0.0210	Defibaugh [38
R40	6.677	416.30	2.7532	0.2682	248.90	0.06211	0.0228	Hsu [39]

4. CALCULATION RESULTS

In this study, the compressibility factors of 18 working fluids were calculated by this four-parameter corresponding-states method using the thermodynamic properties of water, propane, and oxygen. To compare with other four-parameter methods, the PSB model, a four-parameter method with a high accuracy [9], was selected as a reference model, and the predicted results by the reference model were calculated too. When calculating densities, the pressures and temperatures were used as the input variables for the comparisons. The basic parameters of the reference fluids and test fluids are indicated in Table I.

Table II. Comparisons Between Experimental and Calculated Results

	This work		PSB model			Data range		Data source (first author)
Substance	Aad	Bias	Aad	Bias	Number	P_r	T_r	
R152a	1.18	1.12	0.89	0.84	330	0.0236–3.6151	0.7587–1.1210	Tillner-Roth [14]
i-C_4H_{10}	0.96	0.96	0.15	−0.15	30	0.4577–3.8628	0.5394–0.7356	William [15]
R236fa	1.25	1.25	1.27	1.27	42	0.1268–0.3055	0.7888–0.9144	Giovanni [16]
R124	1.56	−0.89	1.81	−0.21	134	0.1168–2.2601	0.2666–1.0700	Boyes [17], Walter [18]
R23	1.36	1.10	0.95	0.46	79	0.0793–2.8494	0.7432–1.3113	Hou [19]
R22	0.59	−0.37	0.32	0.32	40	0.0210–2.8152	0.5614–0.8936	Handel [20], Caustevo [21]
R123	0.97	0.30	1.43	1.28	113	0.4205–3.2586	0.6814–1.1452	Piao [22]
R14	1.30	−1.04	1.65	1.62	285	0.2237–4.5013	0.7030–1.5058	Rubio [23]
R113	0.47	0.12	0.76	0.39	77	0.0020–1.8306	0.5926–1.2311	Martin [24]
R12	0.74	−0.54	1.16	−0.08	190	0.0091–1.9345	0.5193–0.9689	Prasad [25], Handel [20]
R500	0.28	0.19	0.28	0.14	17	0.0270–0.1666	0.8269–1.0910	Prasad [26]
R141b	0.95	−0.95	0.66	−0.66	23	0.1167–0.5176	0.5866–0.8380	Maezawa [27]
R142b	1.09	0.27	1.07	0.71	56	0.2464–2.3191	0.7799–1.0801	Maezawa [28], Yada [29]
R143a	1.03	0.98	0.84	0.80	206	0.0029–3.9852	0.7609–1.1656	Weber [30], Zhang [31]
R134a	0.72	0.50	0.92	0.72	749	0.0136–4.3436	0.5347–1.2767	Hou [32], Piao [33], Tillner-Roth [14], Wilson [34]
CH_4	0.47	0.14	0.57	−0.18	578	0.0212–2.6184	0.5248–1.5384	Pieperbeck [35], Kleinrahm [36], Handel [37]
R245ca	0.09	0.05	1.40	−1.40	317	0.2553–1.6564	0.5430–0.8301	Defibaugh [38]
R40	0.67	0.14	—	—	634	0.0304–4.4767	0.7402–1.1966	Hsu [39]
Overall 1[a]	0.80	0.22	1.01	0.35	3266	0.0020–4.3436	0.5193–1.5058	
Overall 2[b]	0.78	0.21	—	—	3900	0.0020–4.4767	0.5193–1.5058	

[a] The results excluding R40.

[b] The results including R40.

The results calculated by both methods were compared with experimental values. The comparison between experimental and calculated results is indicated in Table II. In Table II, Aad is defined as the absolute average error, and Bias is defined as the average error.

$$\text{Aad} = \sum_{i=1}^{n} \frac{|100 \times (Z_{\text{cal}}/Z_{\text{exp}} - 1)|}{n} \tag{13}$$

$$\text{Bias} = \sum_{i=1}^{n} \frac{100 \times (Z_{\text{cal}}/Z_{\text{exp}} - 1)}{n} \tag{14}$$

In Table II, compared with experimental data, the overall absolute average error of this work, not including R40, is about 0.80%. If we include R40, the overall absolute average error is about 0.78%. The prediction precision is higher than that of the PSB method [9], which has an overall absolute average error (without R40) of about 1.01%.

The deviations between compressibility factors calculated by both the new model and the PSB model and experimental results for R134a are indicated in Figs. 1 and 2, and those of methane in Figs. 3 and 4. According to the specific comparisons in the figures, the larger deviations between

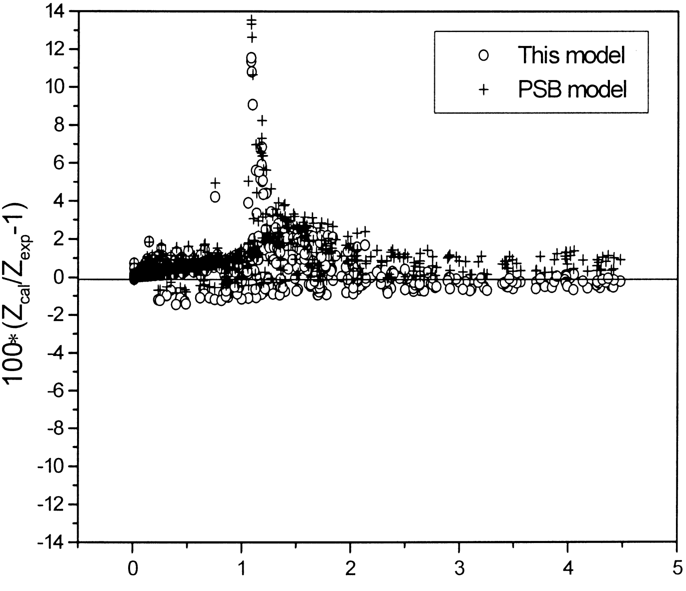

Fig. 1. Deviations for R134a versus P_r.

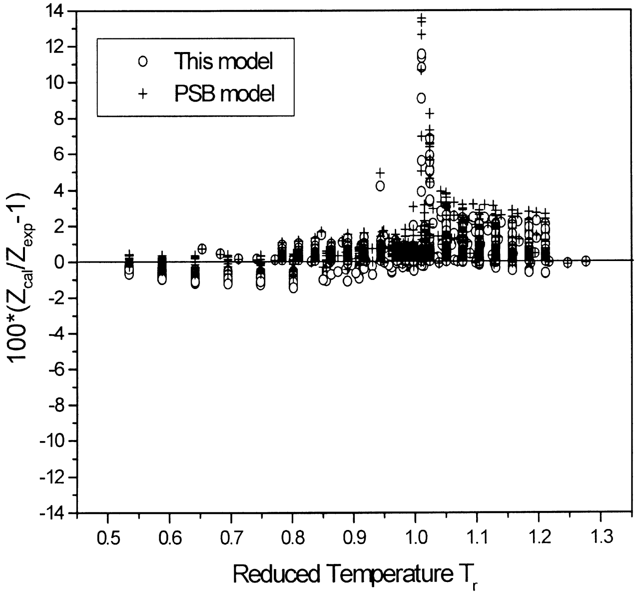

Fig. 2. Deviations for R134a versus T_r.

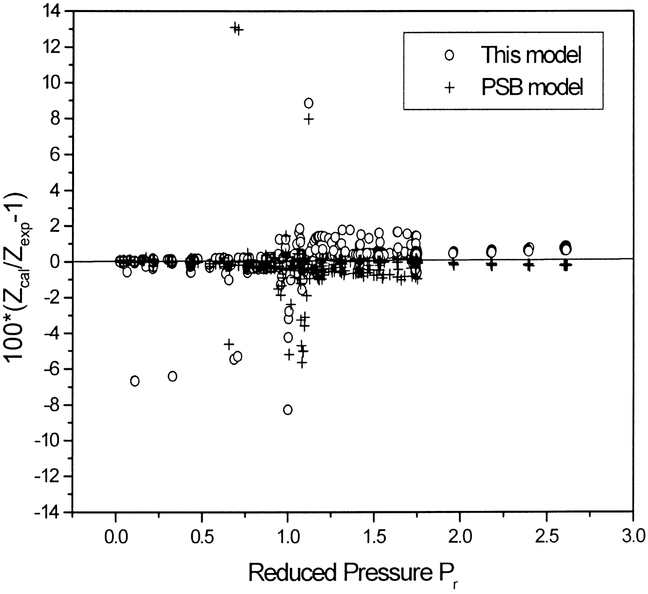

Fig. 3. Deviations for methane versus P_r.

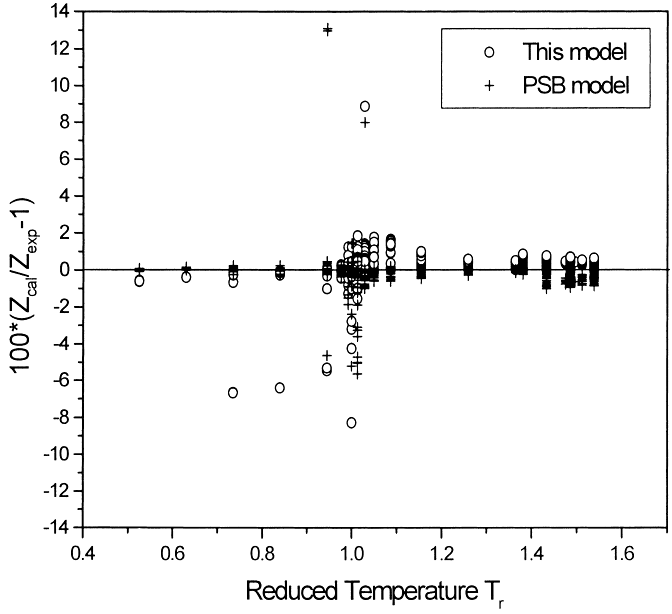

Fig. 4. Deviations for methane versus T_r.

calculated and experimental results appear in the regions near the critical point. There may be three major reasons: (a) the equations of state of the reference substances have larger errors in these regions, (b) the corresponding-states method has unreasonable behavior in these regions, and (c) the experimental data near the critical region have larger errors.

In this work, the overall range of experimental values of the 18 fluids is $0.0020 \leqslant P_r \leqslant 4.4767$ and $0.2666 \leqslant T_r \leqslant 1.5058$. However, the applicability of this method depends mostly on the applicability of the state equations of these reference substances. The more extensive the applicability of the reference equations, the more extensive is the applicability of this method. Therefore, it is very important to select good state equations of the reference substances.

Because the fluids chosen in this study have larger differences, and experiment data cover the entire region including the liquid, gas, near-critical, and supercritical regions, the new method is a good generalized corresponding-states model.

But there is another problem. This method may have larger errors near the saturation line because the property of the fluid's saturation state cannot be exactly predicted by corresponding states. This question should be solved by other methods.

5. CONCLUSION

In this study, a new generalized four-parameter corresponding-states method, which is based on the thermodynamic properties of three kinds of reference substances, is presented. Using this method, the thermodynamic properties of other fluids can be obtained. It is different from other four-parameter corresponding-states methods in that the normal boiling temperature was selected as the third parameter instead of the acentric factor, and the critical compressibility factor was selected as the fourth parameter in the new model.

The calculation results of the new method were compared with 3900 experimental data for 18 fluids. Its absolute average error is about 0.8%, which is better than that of the PSB method. The precision of the new method can satisfy engineering requirements, and the new method uses more common fluid parameters.

The calculation precision of this work indicates that the prediction results near the saturation line and critical point are not perfect, which is a common problem for corresponding states methods. Further investigation should be undertaken to resolve this problem.

ACKNOWLEDGMENT

This project is supported by the National Science Foundation of China (No. 59976040).

REFERENCES

1. Z. S. Chen, W. L. Cheng, and P. Hu, *J. Eng. Thermophys.* **22**:19 (2001) [in Chinese].
2. Z. S. Chen and T. Ito, *Proc. 5th Asia Thermophys. Prop. Conf.*, Seoul (1998), p. 321.
3. Z. S. Chen, and T. Ito, *Proc. 5th Asia Thermophys. Prop. Conf.*, Seoul (1998), p. 519.
4. K. S. Pitzer, D. Z. Lippmann, R. F. Curl, C. M. Huggins, and D. E. Petersen, *J. Am. Chem. Soc.* **77**:3433 (1955).
5. B. I. Lee and M. G. Kesler, *AIChE J.* **21**:510 (1975).
6. G. Z. Wu and L. I. Stiel, *AIChE J.* **31**:1632 (1985).
7. W. V. Wilding and R. L. Rowley, *Int. J. Thermophys.***7**:525 (1986).
8. G. Scalabrin, S. D. Santo, and M. Grigiante, *Proc. 5th Asia Thermophys. Prop. Conf.*, Seoul (1998), p. 325.
9. K. Park, R. E. Sonntag, and C. Borgnakke, *Int. J. Energy Res.* **20**:811 (1996).
10. T. Ito, R. Akasaka, T. Iwamoto, Y. Kato, T. Kuroki, T. Shigechi, Y. Takata, H. Tanigawa, H. Taniguchi, T. Hamatake, T. Fujita, T. Hoda, T. Masuoka, M. Miyamoto, S. Momoki, Y. Yasuda, T. Yamaguchi, H. Yamashita, and K. Yoshioka, *A Program Package for Thermophysical Properties of Fluids*, Version 11.1 (1999).
11. Japan Soc. Mech. Eng., *1980 SI JSME Steam Tables* (1981).
12. K. Bühner, G. Maurer, and E. Bender, *Cryogenics* **21**:157 (1981).

13. V. V. Sychev, A. A. Vasserman, A. D. Kozlov, G. A. Spiridonov, and V. A. Tsymarny, *Thermodynamic Properties of Oxygen, National Standard Reference Data of the USSR: A Series of Property Tables, Vol. 5* (Hemisphere, New York, 1987).
14. R. Tillner-Roth and H. D. Baehr, *J. Chem. Thermodyn.* **24**:413 (1992).
15. M. H. William, *J. Chem. Eng. Data* **28**:367 (1983).
16. D. N. Giovanni, G. Giuliano, and P. Fabio, *J. Chem. Eng. Data* **44**:696 (1999).
17. S. J. Boyes and L. A. Weber, *Int. J. Thermophys.* **15**:443 (1994).
18. B. Walter, K. Gunther, and W. Rolf, *J. Chem. Eng. Data* **41**:476 (1996).
19. Y. C. Hou and J. J. Martin, *AIChE J.* **5**:125 (1959).
20. G. Handel, R. Kleinrahm, and W. Wagner, *J. Chem. Thermodyn.* **24**:697 (1992).
21. A. Caustevo and S. Iglesias, *J. Chem. Eng. Data* **40**:1151 (1995).
22. C.-C. Piao, H. Sato, and K. Watanabe, *J. Chem. Eng. Data* **36**:398 (1991).
23. R. G. Rubio, J. C. G. Calado, P. Clancy, and W. N. Streett, *J. Phys. Chem.* **89**:4637 (1985).
24. J. M. Martin, F. S. Richard, and N. S. Paul, *J. Chem. Eng. Data*, **23**:113 (1978).
25. M. Prasad, *J. Chem. Eng. Data* **26**:361 (1981).
26. M. Prasad and A. P. Kudchadker, *J. Chem. Eng. Data* **23**:190 (1978).
27. Y. Maezawa, H. Sato, and K. Watanabe, *J. Chem. Eng. Data* **36**:151 (1991).
28. Y. Maezawa, H. Sato, and K. Watanabe, *J. Chem. Eng. Data* **36**:148 (1991).
29. N. Yada, T. Kumatsu, H. Sato, and K. Watanabe, *J. Chem. Eng. Data* **36**:12 (1991).
30. L. A. Weber and D. R. Defibaugh, *J. Chem. Eng. Data* **41**:1477 (1996).
31. H.L. Zhang, H. Sato, and K. Watanabe, *J. Chem. Eng. Data* **40**:887 (1995).
32. H. Hou, J. C. Holste, B. E. Gammon, and K. N. Marsh, *Int. J. Refrig.* **15**:365 (1992).
33. C.-C Piao, H. Sato, and K. Watanabe, *ASHRAE Trans.* **96**: 132 (1990), Part 1.
34. D. P. Wilson and R. S. Basu, *ASHRAE Trans.* **94**:2095 (1988), Part 2.
35. N. Pieperbeck, R. Kleinrahm, W. Wagner, and M. Jaeschke, *J. Chem. Thermodyn.* **23**:175 (1991).
36. R. Kleinrahm, W. Duschek, and W. Wagner, *J. Chem. Thermodyn.* **20**:621 (1988).
37. G. Handel, R. Kleinrahm, and W. Wagner, *J. Chem. Thermodyn.* **24**: 685 (1992).
38. D. R. Defibaugh, K. A. Gillis, M. R. Moldover, J. W. Schmidt, and L. A. Weber, *Int. J. Refrig.* **19**:285 (1996).
39. C. C. Hsu and J. J. Mcketta, *J. Chem. Eng. Data* **9**:45 (1964).
40. B. Platzer, A. Polt, and G. Maurer, *Thermophysical Properties of Refrigerants* (Springer-Verlag, New York, 1990).
41. Jpn. Assoc. Refrig., *Thermophysical Properties of Refrigerants (R22, Chlorodifluoromethane)* (1975)
42. S. Angus and K. M. de Reuck, *International Thermodynamic Table of the Fluid State-5 Methane, Vol. 5* (IUPAC, 1976).
43. R. Tillner-Roth, J. Li, A. Yokozeki, H. Sato, and K. Watanabe, *Thermodynamic Properties of Pure and Blended Hydrofluorocarbon (HFC) Refrigerants* (JSRAE, Tokyo, 1997).