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# An Extended Corresponding-States Model for Predicting Thermodynamic Properties of $N_2$–Ar–$O_2$ Mixtures Including Vapor–Liquid Equilibrium[1]

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A formulation developed previously for the prediction of the thermodynamic properties of single-phase states of binary and ternary mixtures in the nitrogen–argon–oxygen system has been revised to include the calculation of vapor–liquid equilibrium (VLE) properties. The model is based on the theory of extended corresponding states with van der Waals mixing rules. Binary interaction parameters have been determined with single-phase $P$–$\rho$–$T$ and vapor–liquid equilibrium data to improve the accuracy of thermodynamic property predictions. The model accurately represents single-phase and vapor–liquid equilibrium properties over a wide range of compositions for binary and ternary mixtures. Comparisons of calculated properties to selected mixture data for both single-phase and VLE states are included.

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**KEY WORDS:** binary interaction parameters; extended corresponding states; shape factors; single-phase $P$–$\rho$–$T$; vapor–liquid equilibrium.

## 1. INTRODUCTION

The need for an accurate wide-range model for predicting thermodynamic properties of fluid mixtures has been well established. Because there is a significant quantity of measured property data for binary and ternary mixtures of nitrogen, argon, and oxygen, these systems may be used for testing methods of property calculation. The model presented here superceeds that done by Clarke et al. [1]. The methods used here for vapor–liquid equilibrium (VLE) calculations were first adapted for use

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with accurate pure-fluid equations of state by Rousseau [2] and were modified by Clarke et al. [3] for use with the model reported in this work. Although there are few sources of data for derived properties of mixtures, the available heat capacity and speed-of-sound data for air provided a means of validating predictions of these properties. The composition of air used in this work is 78.12% nitrogen, 20.96% oxygen, and 0.92% argon, as given by Jacobsen et al. [4].

## 2. EXTENDED CORRESPONDING-STATES (ECS) MODEL FOR MIXTURES

The equations of state used in this work for calculation of pure-fluid properties are those of Jacobsen et al. [5] for nitrogen, Schmidt and Wagner [6] for oxygen, and Stewart and Jacobsen [7] for argon. The model used in this research is described in detail by Clarke [8] and by Clarke et al. [1]. Essential details of the formulation by Clarke et al. [1] are repeated here.

Extended corresponding-states theory can be generalized to predict thermodynamic properties of a mixture by assuming that the mixture behaves as a hypothetical equivalent pure substance. The extension of the one-fluid theory to mixtures uses van der Waals mixing rules. Corresponding states for the mixture are defined by the equations

$$\bar{\alpha}_{\mathrm{m}}(\delta_{\mathrm{m}}, \tau_{\mathrm{m}}) = \bar{\alpha}_{\mathrm{o}}(\delta_{\mathrm{o}}, \tau_{\mathrm{o}}) = \bar{\alpha}_{\mathrm{o}}(\delta_{m}\phi_{\mathrm{m}}, \tau_{\mathrm{m}}\theta_{\mathrm{m}}) \tag{1}$$

$$Z_{\mathrm{m}}(\delta_{\mathrm{m}}, \tau_{\mathrm{m}}) = Z_{\mathrm{o}}(\delta_{\mathrm{o}}, \tau_{\mathrm{o}}) = Z_{\mathrm{o}}(\delta_{\mathrm{m}}\phi_{\mathrm{m}}, \tau_{\mathrm{m}}\theta_{\mathrm{m}}) \tag{2}$$

where $\bar{\alpha}$ is the residual Helmholtz energy, $Z$ is the compressibility factor, $\delta = (\rho/\rho_{\mathrm{c}})$ is the reduced density, $\tau = (T_{\mathrm{c}}/T)$ is the reciprocal reduced temperature, the subscript c indicates a critical property, the subscript o refers to the reference fluid, and the subscript m refers to the mixture. The symbols $\phi_{\mathrm{m}}$ and $\theta_{\mathrm{m}}$ are shape factors which are used to relate the reduced properties of the mixture to those of the reference fluid.

The thermodynamic properties for the mixture are reduced by the parameters, $\rho_{\mathrm{cm}}$ and $T_{\mathrm{cm}}$, which are given by

$$\rho_{\mathrm{cm}} = \left[\sum_{p}\sum_{q}\left(\frac{x_p x_q}{\rho_{\mathrm{c}qp}}\right)\right]^{-1} \tag{3}$$

$$T_{\mathrm{cm}} = \frac{\displaystyle\sum_{p}\sum_{q} x_p x_q T_{\mathrm{c}pq}/\rho_{\mathrm{c}pq}}{\displaystyle\sum_{p}\sum_{q} x_p x_q/\rho_{\mathrm{c}pq}} \tag{4}$$

where $p$ and $q$ are indices which refer to different mixture components.

In Eqs. (3) and (4), $\rho_{cpq}$ and $T_{cpq}$ are given by

$$\rho_{cpq} = 8\left[\left(\frac{1}{\rho_{cp}}\right)^{1/3} + \left(\frac{1}{\rho_{cq}}\right)^{1/3}\right]^{-3} \tag{5}$$

$$T_{cpq} = (T_{cp}T_{cq})^{1/2} \tag{6}$$

The shape factors $\phi_m$ and $\theta_m$ for the mixture are given by

$$\phi_m = \sum_p \sum_q x_p x_q \phi_{pq} \tag{7}$$

$$\theta_m = \sum_p \sum_q x_p x_q \theta_{pq} \phi_{pq} \tag{8}$$

The combining rules for the calculation of $\phi_{pq}$ and $\theta_{pq}$ are given by

$$\phi_{pq} = \frac{\eta_{pq}}{8}\left[\left(\frac{\phi_p \rho_{cm}}{\rho_{cp}}\right)^{1/3} + \left(\frac{\phi_q \rho_{cm}}{\rho_{cq}}\right)^{1/3}\right]^3 \tag{9}$$

$$\theta_{pq} = \xi_{pq}\left[\left(\frac{\theta_p T_{cp}}{T_{cm}}\right)\left(\frac{\theta_q T_{cq}}{T_{cm}}\right)\right]^{1/2} \tag{10}$$

Exact shape factors, $\phi_p$, $\phi_q$, $\theta_p$, and $\theta_q$, were determined by simultaneous solution of equations similar to Eqs. (1) and (2) for the residual Helmholtz energy and compressibility factors for each pure fluid with nitrogen as the reference fluid. The binary interaction parameters, $\eta_{pq}$ and $\xi_{pq}$, are represented by linear combinations of temperature as explained by Clarke [8]:

$$\eta_{pq} = a_{pq} + \frac{b_{pq}}{\tau_m} \tag{11}$$

$$\xi_{pq} = c_{pq} + \frac{d_{pq}}{\tau_m} \tag{12}$$

The values of the coefficients for Eqs. (11) and (12) determined by nonlinear least-squares fitting of experimental data are listed in Table I.

**Table I.** Coefficients for Temperature-Dependent Binary Interaction Parameters

| Binary | $p, q$ | $a_{pq}$ | $b_{pq}$ | $c_{pq}$ | $d_{pq}$ |
|---|---|---|---|---|---|
| $N_2$-$O_2$ | 1, 3 | 1.00841 | −0.00512481 | 0.998398 | 0.00698625 |
| $N_2$-Ar | 1, 2 | 1.01078 | −0.00788505 | 0.989402 | 0.0146454 |
| Ar-$O_2$ | 2, 3 | 1.00637 | 0.0 | 0.991117 | 0.0 |

**Table II.** Selected Single-Phase Mixture Data for $N_2$–Ar–$O_2$ Mixtures

| Author | Year | No. of points | $T$ range (K) | AAD (%) | BIAS (%) |
|---|---|---|---|---|---|
| Nitrogen–oxygen ($P$–$\rho$–$T$) | | | | | |
| Blagoi & Rudenko [10] | 1958 | 19 | 67–79 | 0.400 | 0.400 |
| Knaap et al. [11] | 1961 | 7 | 76.9 | 0.078 | 0.075 |
| Pool et al. [12] | 1962 | 7 | 83.8 | 0.130 | 0.130 |
| Summary | | 33 | 67–83.8 | 0.274 | 0.235 |
| Nitrogen–argon ($P$–$\rho$–$T$) | | | | | |
| Crain & Sonntag [13] | 1966 | 264 | 143–273 | 0.193 | 0.067 |
| Palavra [14] | 1979 | 203 | 94–106 | 0.075 | 0.075 |
| Pool et al. [12] | 1962 | 24 | 83.8 | 0.427 | −0.401 |
| Ricardo et al. [15] | 1992 | 21 | 119 | 0.143 | 0.112 |
| Townsend [16] | 1956 | 144 | 298, 323 | 0.053 | −0.020 |
| Zandbergen & Beenakker [17] | 1967 | 55 | 170–292 | 0.163 | −0.118 |
| Summary | | 711 | 83.8–323 | 0.135 | 0.023 |
| Argon–oxygen ($P$–$\rho$–$T$) | | | | | |
| Blagoi & Rudenko [10] | 1958 | 36 | 70–89 | 0.296 | 0.116 |
| Knaap et al. [11] | 1961 | 6 | 90 | 0.037 | 0.029 |
| Pool et al. [12] | 1962 | 15 | 84, 90 | 0.012 | −0.001 |
| Saji & Okuda [18] | 1965 | 20 | 84, 87 | 0.246 | 0.002 |
| Summary | | 77 | 70–90 | 0.208 | 0.057 |
| Air ($P$–$\rho$–$T$) | | | | | |
| Blanke [19] | 1977 | 130 | 61–170 | 0.257 | 0.117 |
| Howley & Magee [20] | 1990 | 286 | 67–400 | 0.102 | 0.078 |
| Kozlov [21] | 1968 | 348 | 288–873 | 0.069 | −0.016 |
| Michels et al. [22] | 1954 | 157 | 118–248 | 0.035 | 0.024 |
| Michels et al. [23] | 1954 | 199 | 273–348 | 0.148 | 0.044 |
| Romberg [24] | 1971 | 124 | 84–122 | 0.093 | 0.093 |
| Summary | | 1244 | 61–873 | 0.107 | 0.045 |
| Air (speed of sound) | | | | | |
| Ewing & Goodwin [25] | 1988 | 13 | 255 | 0.005 | −0.003 |
| Van Itterbeek & de Rop [26] | 1955 | 14 | 229–313 | 0.211 | 0.137 |
| Younglove & Frederick [27] | 1992 | 169 | 90–300 | 0.366 | −0.307 |
| Summary | | 226 | | 0.315 | −0.203 |
| Air (heat capacity) | | | | | |
| Magee [28] | 1992 | 231 | 66–300 | 0.638 | 0.426 |

**Table III.** Selected VLE Data for $N_2$-Ar-$O_2$ Mixtures

| Author | Year | No. of points | $T$ range (K) | AAD (%) | BIAS (%) |
|---|---|---|---|---|---|
| Nitrogen–oxygen | | | | | |
| Armstrong et al. [29] | 1955 | 70 | 65–78 | 0.590 | 0.101 |
| Duncan & Staveley [30] | 1966 | 11 | 63 | 0.754 | 0.753 |
| Hiza [31] | 1990 | 63 | 63–100 | 0.688 | −0.510 |
| Pool et al. [12] | 1962 | 11 | 84 | 0.214 | −0.035 |
| Wilson et al. [32] | 1965 | 138 | 78–136 | 0.079 | −0.691 |
| Summary | | 293 | 63–136 | 0.696 | −0.384 |
| Nitrogen–argon | | | | | |
| Hiza [31] | 1990 | 36 | 85–100 | 0.210 | 0.128 |
| Narinskii [33] | 1966 | 98 | 80–120 | 0.469 | −0.001 |
| Pool et al. [12] | 1962 | 12 | 83.82 | 0.428 | 0.357 |
| Thorpe [34] | 1966 | 68 | 80–116 | 0.789 | 0.725 |
| Wilson et al. [32] | 1965 | 183 | 72–134 | 0.853 | −0.717 |
| Summary | | 397 | 72–134 | 0.673 | −0.174 |
| Argon–oxygen | | | | | |
| Burn & Din [35] | 1962 | 140 | 84–118 | 0.874 | 0.864 |
| Clark et al. [36] | 1953 | 55 | 90–110 | 0.403 | 0.374 |
| Hiza [31] | 1990 | 16 | 95–100 | 0.606 | −0.202 |
| Narinskii [37] | 1957 | 55 | 90–121 | 0.379 | 0.270 |
| Pool et al. [12] | 1962 | 24 | 84–90 | 1.877 | 0.334 |
| Wilson et al. [32] | 1966 | 200 | 87–139 | 0.402 | −0.064 |
| Summary | | 490 | 84–139 | 0.597 | 0.314 |

An iterative procedure was used to determine $\delta_o$ and $\tau_o$ given $\delta_m$ and $\tau_m$. Convergence of the iteration required that the mixture and its components be in corresponding states with the selected reference fluid at $\delta_o$ and $\tau_o$. All thermodynamic properties of the constant-composition mixture may be calculated from $\bar{\alpha}(\delta_m, \tau_m)$ and its derivatives with respect to the independent variables, $\delta_m$ and $\tau_m$. Details of these property calculations are given by Clarke [8].

Vapor–liquid equilibrium properties are calculated using procedures outlined by Rousseau [2] and adapted to the model described above. Calculations may be performed for mixtures by specifying various combinations of properties for either the liquid phase, the vapor phase, or the bulk fluid. The thermodynamic constraints for vapor–liquid equilibrium are equal temperature, pressure, and fugacity in the liquid and vapor phases, respectively. The equation for fugacity is

$$f_i = \rho RT \exp\left(\frac{\partial(n\bar{a})}{\partial n_i}\right)_{T,V,n_{j\neq i}} \tag{13}$$

where $f$ is the fugacity, $n$ is the number of moles, and $V$ is the total volume.

## 3. COMPARISONS OF CALCULATED MIXTURE PROPERTIES TO EXPERIMENTAL DATA

The extended corresponding-states model was used to calculate single-phase mixture properties for individual states at specified temperature, pressure, and molar composition. Available experimental $P$–$\rho$–$T$ data for mixtures in the nitrogen–argon–oxygen system were used as the basis for

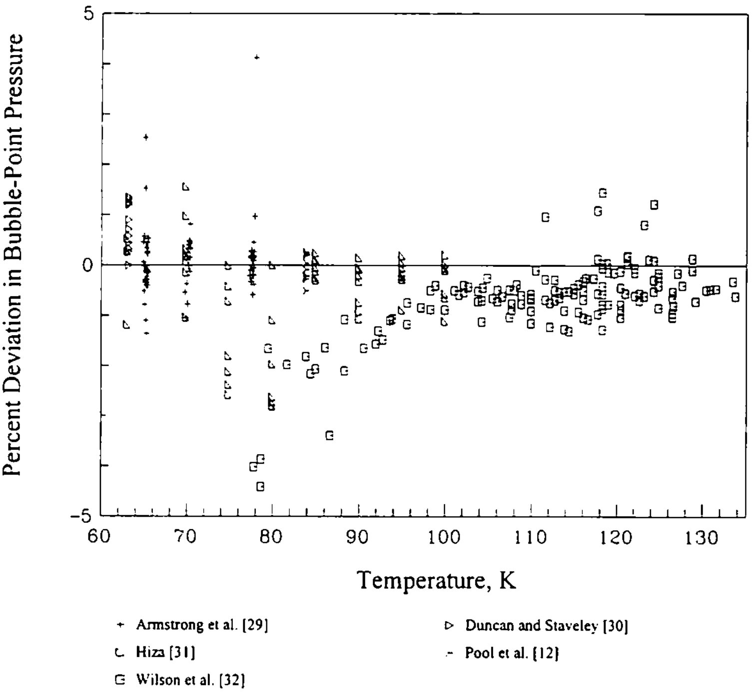

**Fig. 1.** Percentage deviation in bubble-point pressure between selected experimental data for the nitrogen–oxygen binary mixture and calculations from the ECS model.

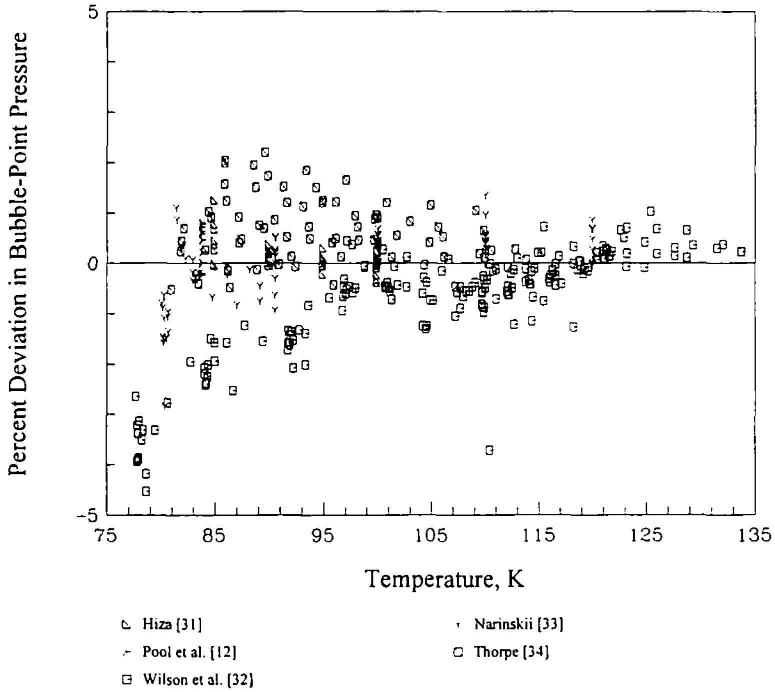

**Fig. 2.** Percentage deviations in bubble-point pressure between selected experimental data for the nitrogen-argon binary mixture and calculations from the ECS model.

the comparisons. For VLE, deviations of values determined with the ECS model from experimental bubble-point pressures were calculated at specified temperatures and liquid compositions. Nitrogen was used as the reference fluid.

The percentage deviation in a property, $x$, is defined as

$$\% \Delta x = 100\left(\frac{x_{\text{data}} - x_{\text{calc}}}{x_{\text{data}}}\right) \tag{14}$$

The average absolute deviation (AAD) is given by

$$\text{AAD} = \frac{\sum |\% \Delta x|}{n} \tag{15}$$

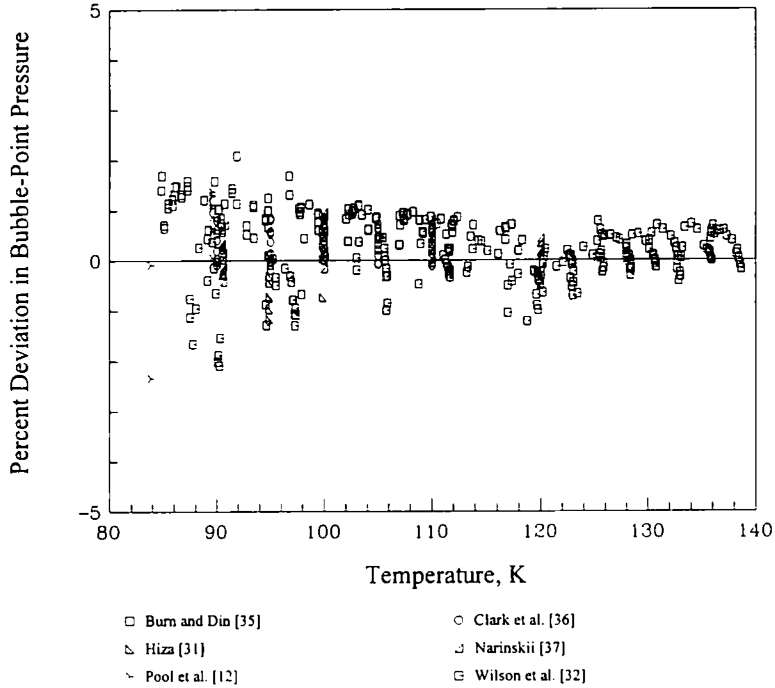

Fig. 3. Percentage deviation in bubble-point pressure between selected experimental data for the argon–oxygen binary mixture and calculations from the ECS model.

where $n$ is the number of data points. The bias value is the arithmetic mean of the percentage deviation,

$$\text{BIAS} = \frac{\sum (\%\ \Delta x)}{n} \tag{16}$$

Tables II and III summarize data for $N_2$–Ar–$O_2$ mixtures selected for the reported comparisons. Table II lists the sources and ranges of single-phase mixture data as well as summary comparisons of the calculated densities to experimental densities. Table III lists VLE data for mixtures of various compositions as well as summary comparisons of calculated bubble-point pressures to experimental bubble-point pressures.

Figures 1 to 3 show the differences between selected VLE data and calculations from the ECS model. These comparisons indicate that calculated pressures are within ±1% of the experimental values selected for the determination of the coefficients of Eqs. (11) and (12). The deviations for all the available data range between −5 and +3% in pressure. Comparisons of properties predicted by the ECS model with $P$–$\rho$–$T$ data for air are usually within ±0.2% in density, except in the critical region and for low-temperature liquid states where the density exceeded 30 mol · dm$^{-3}$. For liquid states below 75 K, the density differences are less than ±0.5%. In this region, the larger density deviations may be caused by anomalous behavior of the pure-fluid equations near their triple points. Comparisons to heat capacity and sound speed data for air are within ±1%.

## REFERENCES

1. W. P. Clarke, R. T Jacobsen, S. W. Beyerlein, and S. G. Penoncello, *Fluid Phase Equil.* **88**:13 (1993).
2. M. F. Rousseau, *Prediction of Properties of Nitrogen-Argon-Oxygen Mixtures Using Extended Corresponding States Methods*, M.S. thesis (University of Idaho, Moscow, 1988).
3. W. P. Clarke, M. F. Rousseau, and R. T Jacobsen, *Phase Equilibrium Method for Binary and Ternary Mixtures (Applications to the Nitrogen-Oxygen-Argon System)*, Report 88-1 (Center for Applied Thermodynamic Studies, University of Idaho, Moscow, 1988).
4. R. T Jacobsen, S. G. Penoncello, S. W. Beyerlein, W. P. Clarke, and E. W. Lemmon, *Fluid Phase Equil.* **79**:113 (1992).
5. R. T Jacobsen, R. B. Stewart, and M. Jahangiri, *J. Phys. Chem. Ref. Data* **15**(2):735 (1986).
6. R. Schmidt and W. Wagner, *Fluid Phase Equil.* **19**:175 (1985).
7. R. B. Stewart and R. T Jacobsen, *J. Phys. Chem. Ref. Data* **18**(2):639 (1989).
8. W. P. Clarke, *Thermodynamic Properties of* $N_2$ *Ar* $O_2$ *Mixtures from an Extended Corresponding States Model*, M.S. thesis (University of Idaho, Moscow, 1990).
9. E. W. Lemmon, R. T Jacobsen, and S. W. Beyerlein, *Adv. Cryo. Eng.* **37B**:1107 (1992).
10. Y. P. Blagoi and N. S. Rudenko, *Izvest. Vyssh. Uchebn. Zaved. Fiz.* **6**:145 (1958).
11. H. F. P. Knaap, M. Knoester, and J. J. M. Beenakker, *Physica* **27**:309 (1961).
12. R. A. H. Pool, G. Saville, T. M. Herrington, D. B. C. Shields, and L. A. K. Staveley, *Trans. Faraday Soc.* **58**:1692 (1962).
13. R. W. Crain, Jr., and R. E. Sonntag, *Adv. Cryo. Eng.* **11**:379 (1966).
14. A. M. F. Palavra, *Efeito da Pressão e da Temperatura Sobre as Funções de Excesso do Sistema Argon-azoto*, Ph.D. thesis (Institute Superior Técnico, Universidade Técnica de Lisboa, 1979).
15. A. A. Ricardo, S. F. Barreiros, M. Nunes da Ponte, G. M. N. Albuquerque, and J. C. G. Calado, *J. Chem. Thermodyn.* **24**:1281 (1992).
16. P. W. Townsend, *Pressure-Volume-Temperature Relationship of Binary Gaseous Mixtures*, Ph.D. thesis (Columbia University, New York, 1956).
17. P. Zandbergen and J. J. M. Beenakker, *Physica* **33**(2):343 (1967).
18. Y. Saji and T. Okuda, *Adv. Cryo. EDng.* **10**:209 (1965).
19. W. Blanke, *Messung der thermischen Zustandgrossen von Luft im Zweiphasengebeit und seiner Umgebung*, Ph.D. dissertation (Ruhr University, Bochum, Germany, 1973).
20. J. B. Howley and J. Magee, private communication (1990).
21. A. Kozlov, *Experimental Investigation of the Specific Volumes of Air in the 20-600 C Temperature Range and 20-700 Bar Pressure Range*, Ph.D. dissertation (Moscow Power Engineering Institute, Moscow, 1968).

22. A. Michels, T. Wassenaar, J. M. H. Levelt Sengers, and W. De Graaf, *Appl. Sci. Res.* **A4**:381 (1954).
23. A. Michels, T. Wassenaar, and W. Van Seventer, *Appl. Sci. Res.* **A4**:52 (1954).
24. H. Romberg, VDI, Forschungsheft 543, Düsseldorf (1971).
25. M. B. Ewing and A. R. H. Goodwin, *J. Chem. Thermodyn.* **25**:423 (1988).
26. A. Van Itterbeek and W. de Rop, *Appl. Sci. Res.* **A6**:21 (1955).
27. B. A. Younglove and N. V. Frederick, *Int. J. Thermophys.* **13**(6):1033 (1992).
28. J. W. Magee, private communication (1992).
29. G. T. Armstrong, J. M. Goldstein,. and D. E. Roberts, *J. Res. Natl. Bur. Stand.* **55**(5):265 (1955).
30. A. G. Duncan and L. A. K. Staveley, *Trans. Faraday Soc.* **62**:548, Part 3 (1966).
31. M. J. Hiza, private communication (1990).
32. G. M. Wilson, P. M. Silverberg, and M. G. Zellner, *Adv. Cryo. Eng.* **10**:192 (1965).
33. G. B. Narinskii, *Russ. J. Phys. Chem.* **40**(9):1093 (1966).
34. P. L. Thorpe, *Trans. Faraday Soc.* **64**(549):2273, Part 9 (1968).
35. I. Burn and F. Din, *Trans. Faraday Soc.* **58**:1341, Part 1 (1962).
36. A. M. Clark, F. Din, and J. Robb, *Proc. R. Soc. London* **A221**(A):517 (1954).
37. G. B. Narinskii, *Kislorodnyi* **10**(3):9 (1957).