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A Thermodynamic Property Formulation for Air. II. Pressure and Density Estimation Functions for the Dew and Bubble Lines[1]

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As a companion to a new correlation for the thermodynamic properties of air in single-phase states, new values for the properties on the dew and bubble lines have been calculated. Phase equilibrium properties for air at low and moderate pressures were predicted from accurate equations of state for argon, nitrogen, and oxygen using extended corresponding-states (ECS) methods. For pressures near the critical pressure, property values were calculated using a modified Leung–Griffiths model for mixtures of argon, nitrogen, and oxygen. Available experimental data and newly predicted values have been used in developing new correlating functions for estimating density and pressure on the dew and bubble lines of air. Estimates of the accuracies of these correlations based upon comparisons of calculated properties to data from other sources are also included.

KEY WORDS: air; bubble point; dew point; phase equilibrium; thermodynamic properties.

1. INTRODUCTION

This paper is a companion to the preceding paper [1], which presents a revised wide-range model for the thermodynamic surface of state of air. For the wide-range model of Jacobsen et al. [1], dry air was considered to

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be a ternary mixture, with mole fractions of 0.7812 N_2, 0.2096 O_2, and 0.0092 Ar, and was treated as a pseudopure substance over the range of single-phase liquid and vapor states where composition remains constant. The correlations for dew- and bubble-line properties of air presented in this work were developed in conjunction with the wide-range model of Ref. 1.

There is considerable uncertainty about the correct shapes of the dew and bubble lines of air in the vicinity of the critical point because this region has not been defined by experiment. Consequently, the theoretical model from Ref. 2 has been extended to ternary mixtures and applied to the nitrogen–argon–oxygen system for the purpose of calculating vapor–liquid equilibrium (VLE) in the critical region of air. Dew- and bubble-line properties for air based on the ternary Leung–Griffiths model are presented in Section 2 and supersede those published in the previous work of Ref. 2, where air was treated as a binary mixture of oxygen and nitrogen. The inclusion of argon in the model has made a small but significant difference in the dew- and bubble-line properties for air.

Another mixture property formulation for the coexistence states of air is the extended corresponding-states model given by Rousseau [3]. This model exhibits significant deviations from the experimental data of Blanke [4] and is used in this work for comparison purposes only.

2. THE MODIFIED LEUNG–GRIFFITHS MODEL FOR AIR

The Leung–Griffiths model [5] as modified by Moldover, Rainwater, and co-workers [6–11] has provided accurate VLE correlations in the critical regions of many binary mixtures. In a previous application, Rainwater and Jacobsen [2] estimated the coexistence properties of air at temperatures above 120 K using a correlation for nitrogen–oxygen mixtures based on the modified Leung–Griffiths model. In this prior work, air was considered to be a mixture with mole fractions of 0.7814 N_2 and 0.2186 O_2. Pressure, density, and temperature values corresponding to state points on the dew and bubble lines were calculated from the model and used as estimates of the coexistence properties of air. Errors in these calculated coexistence properties caused by neglecting the presence of argon and other constituents were ignored.

Rainwater recently extended the formalism of the Leung–Griffiths model to ternary mixtures. In this work, the ternary model was applied to mixtures in the nitrogen–argon–oxygen system using an interpolation scheme developed by Van Poolen. Data of Wilson et al. [12], Jones and Rowlinson [13], and Israel et al. [14] were employed in developing this model. New estimates for coexistence properties of air above 120 K, including estimates of the critical point, maxcondentherm, and maxcondenbar, were calculated using the resulting correlation. These calculated data are listed in Table I. A detailed description of the ternary Leung–Griffiths model is given by Rainwater and Van Poolen [15].

Figure 1 illustrates the phase boundaries near the critical point of air as predicted by the ternary model. The critical point, maxcondentherm,

Table I. P–ρ–T Values for Air Near the Critical Point

Pressure (MPa)	Temperature (K)	Density ($mol \cdot dm^{-3}$)
	Dew line	
3.7860[a]	132.5168[a]	11.8308[a]
3.78909[b]	132.58970[b]	11.094825[b]
3.78905	132.5957	11.0154
3.7871	132.6149	10.6277
3.78502[c]	132.61738[c]	10.44770[c]
3.7755	132.5992	9.9902
3.7361	132.4399	9.1238
3.5907	131.6802	7.7210
3.3863	130.4775	6.6294
3.1899	129.2309	5.8772
3.0019	127.9639	5.2894
2.8221	126.6853	4.8023
2.6503	125.3996	4.3844
2.4861	124.1104	4.0178
2.3295	122.8197	3.6909
2.1800	121.5295	3.3959
	Bubble line	
3.7860[a]	132.5168[a]	11.8308[a]
3.7788	132.4194	12.6480
3.7719	132.3539	13.0390
3.7522	132.1966	13.6873
3.7017	131.8401	14.5838
3.5392	130.7497	16.0909
3.3232	129.2813	17.3314
3.1204	127.8479	18.2328
2.9286	126.4328	18.9702
2.7466	125.0296	19.6072
2.5737	123.6352	20.1753
2.4093	122.2478	20.6926
2.2529	120.8664	21.1706
2.1042	119.4896	21.6170

[a] Critical point.
[b] Maxcondenbar.
[c] Maxcondentherm.

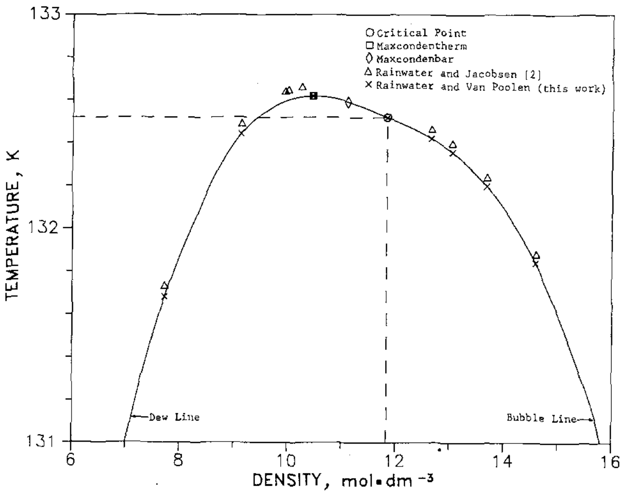

Fig. 1. Coexistence curves for air in the critical region. Solid curves were calculated from a spline fit to the data from Table I.

and maxcondenbar for this mixture do not coincide as they do for a pure fluid. These points are illustrated for air in Fig. 1. Several coexistence states predicted by the older model of Rainwater and Jacobsen [2] are included for comparison. As anticipated, the dew and bubble curves predicted by these two models are in close agreement. As in the previous work of Ref. 2, coexistence properties calculated from the modified Leung–Griffiths model were used in the development of correlating functions for estimating properties on the dew and bubble curves of air. These ancillary equations are described in Section 3.

3. NEW ANCILLARY EQUATIONS FOR THE DEW- AND BUBBLE-LINE PROPERTIES OF AIR

This section presents six ancillary functions for estimating P–ρ–T properties on the dew and bubble lines of air. The two equations presented in Section 3.1 represent pressure as a function of temperature for all coexistence states of air above 60 K. The dew-line equation represents pressure on the dew line up to the maxcondentherm. The bubble-line equation represents all bubble-line states above 60 K and the dew-line states between the critical point and the maxcondentherm. The four equations presented in Section 3.2 relate temperature and density on the dew and bubble lines of air. Two of the four density equations are restricted to the critical region where they give accurate properties for the coexistence states of air and incorporate a new functional form developed for correlating high-pressure VLE data. The other two density equations have ranges of application that are identical to those given for the pressure equations in Section 3.1.

3.1. Dew- and Bubble-Line Pressures

The functional form used for dew- and bubble-line pressures as functions of temperature is

$$[\ln(P/P_j)](T/T_j) = \sum_{i=1}^{25} N_i[1-(T/T_j)]^{i/2} \tag{1}$$

where P_j and T_j are the pressure and temperature at the maxcondentherm point. The coefficients of Eq. (1) for dew- and bubble-line pressures were determined using a least-squares fitting procedure originally developed by Wagner [22] and modified by de Reuck and Armstrong [23]. This fitting procedure chooses terms for Eq. (1) from a bank of 25 candidate terms using statistical tests to determine which combination of terms best represents the data.

Data used to determine the coefficients for Eq. (1) were selected from the sources given in Table II. The only experimental data used were taken from Blanke [4]. These experimental points spanned the entire dew and bubble lines of air. In the critical region, some data calculated from the

Table II. Sources of Dew- and Bubble-Line Properties for Air

Source	Year	Temperature range (K)	Method
Blanke [4]	1973	60–132	Measurement
Michels et al. [19]	1954		Measurement
Bender [16]	1973	65–132	Mixture equation of state
Becker [17]	1982	65–130	Mixture equation of state
Rousseau [3]; Clarke et al. [18]	1988	65–128	ECS prediction
Sychev et al. [20]	1987	60–132	Correlation
Blanke and Weiss [21]	1987	60–132	Correlation
Rainwater and Jacobsen [2]	1988	121–132	Leung–Griffiths model
Rainwater and Van Poolen[a]	1988	119–133	Leung–Griffiths model

[a] Ternary extension of the Leung–Griffiths model described in Section 2.

Table III. Numerical Values for the Coefficients and Exponents for the Bubble- and Dew-Line Equations for Air

Bubble line			Dew line		
Pressure Eq. (1)					
Term	N_i	i	Term	N_i	i
1	0.2087973343	1	1	−0.1385627676	1
2	−6.749760026	2	2	−6.033263552	2
3	2.876398725	3	3	3.906858435	3
4	−1.696557952	4	4	−10.49579778	4
5	12.88978561	25	5	40.26888763	6
			6	−43.17124929	7
			7	0.2218702822×10^{5}	23
			8	$-0.5406773789\times10^{5}$	24
			9	0.3307812761×10^{5}	25
Density Eq. (2)					
Term	C_i	i	Term	C_i	i
1	$-0.3235980762\times10^{-1}$	3	1	$0.4027863775\times10^{-1}$	3
2	$0.6568954182\times10^{-2}$	4	2	$0.1577040421\times10^{-1}$	4
3	$-0.1529793417\times10^{-2}$	5	3	$0.5920058955\times10^{-2}$	5
4	$0.2460774861\times10^{-3}$	6	4	$0.1280454844\times10^{-2}$	6
5	$-0.2378789343\times10^{-4}$	7	5	$0.1597918813\times10^{-3}$	7
6	$0.1256548147\times10^{-5}$	8	6	$0.1059681062\times10^{-4}$	8
7	$-0.2790120452\times10^{-7}$	9	7	$0.2906746577\times10^{-6}$	9
$b_1 = -0.1093$					
$b_2 = 0.010736$					
Density Eq. (3)					
Term	N_i	i	Term	N_i	i
1	−4.9267876271	1	1	−3.856677681	1
2	0.1559599875×10^{3}	2	2	4.209087405	2
3	$-0.1509478314\times10^{4}$	3	3	$-0.1843625686\times10^{3}$	4
4	0.8155523300×10^{4}	4	4	0.6867074827×10^{4}	6
5	$-0.2738210025\times10^{5}$	5	5	$-0.3510380199\times10^{5}$	7
6	0.5939971940×10^{5}	6	6	0.8079003966×10^{5}	8
7	$-0.8341955801\times10^{5}$	7	7	$-0.9322361221\times10^{5}$	9
8	0.7328227178×10^{5}	8	8	0.4451887222×10^{5}	10
9	$-0.3661526794\times10^{5}$	9	9	$-0.1364190836\times10^{5}$	15
10	0.7943581081×10^{4}	10	10	0.1010410721×10^{5}	16

ternary Leung–Griffiths model were included in the fit. These data are listed in Table I. Coefficients for Eq. (1) are given in Table III.

3.2. Dew- and Bubble-Line Densities

The dew- and bubble-point densities for air are represented by four separate ancillary equations. Coefficients for all ancillary equations were determined by least-squares fitting of selected data using the algorithm described earlier. The selection of these alternate equations for specific applications should be based upon consideration of desired accuracy and speed of calculation.

The complex nature of the ternary mixture behavior near the critical point of air has not been well defined by measurement, and the basis of the model provided here for the near-critical region is the modified Leung–Griffiths model of Section 2. Two models are used in this work. A new restricted-range model for dew- and bubble-point densities in the range of temperatures above 121 K, centered on the critical point, provides more accurate results for the densities in this range than the wide-range (60–132 K) functions which were used in the prior work of Rainwater and Jacobsen [2]. Attempts to use these functions for representation of air properties at lower temperatures, however, were unsuccessful.

The ancillary functions presented here have not been constrained to match at the boundaries in the region of overlap in the ranges of validity. Attempts to force matching of these functions resulted in an unacceptable loss of accuracy in the wide-range representation.

The restricted-range model for coexisting densities at temperatures greater than 120 K is

$$\Delta T = b_1 \Delta\rho + b_2 \Delta\rho^2 + \sum_{i=3}^{7} C_i \Delta\rho^i \tag{2}$$

where ΔT is $T - T_c$ and $\Delta\rho$ is $\rho - \rho_c$. The function given in Eq. (2) was developed by Rainwater [24] by expanding the modified Leung–Griffiths model about the critical point of a mixture. Coefficients b_1 and b_2 were determined from theoretical considerations and are the same for both dew and bubble lines. The remaining coefficients, C_i, for dew- and bubble-line densities of air were determined by fitting to the calculated data listed in Table I. These coefficients for temperature in K and for density in $\text{mol} \cdot \text{dm}^{-3}$ are given in Table III.

The wide-range model for the ancillary equation for dew- and bubble-point densities of air is

$$\ln(\rho/\rho_j) = \sum_{i=1}^{25} N_i [1 - (T/T_j)]^e \tag{3}$$

where ρ_j and T_j are the density and temperature at the maxcondentherm point. The exponent e is $i/3$ for the bubble-point values and $i/2$ for the dew-point values. The coefficients for estimating dew- and bubble-line densities of air using Eq. (3) in the temperature range from 60 to 132 K were determined by least-squares fits to the experimental data of Blanke [4] and the calculated data listed in Table I. These coefficients for selected terms are given in Table III.

4. COMPARISONS OF CALCULATED PROPERTIES FROM ANCILLARY EQUATIONS TO VALUES FROM OTHER SOURCES

The assessment of the accuracy of a correlation is generally accomplished by direct comparison to experimental data. In this work, because of the scarcity of experimental data, the comparisons given here are based upon both measured and calculated values. Generally the ancillary equations represent the values selected for their determination within the estimated uncertainty of the data used in the correlation. The comparisons of values calculated using the ancillary equations to selected values, including those used in determining the coefficients in Table III, are given in Figs. 2 and 3. Figure 2 indicates that the uncertainties of dew- and bubble-point pressures calculated from Eq. (1) are $\pm 0.2\%$ for the entire range from 60 K to the maxcondentherm. Uncertainties of dew- and bubble-point densities calculated from Eq. (3) are $\pm 0.2\%$ in the temperature range from 60 to 110 K. Above 110 K, systematic deviations of calculated dew-line densities from the data of Blanke [4] and Michels [19] are evident. The experimental data of Blanke [4] and the predicted values from the Rainwater and Van Poolen model (this work) do not agree in this region, so an uncertainty as high as $\pm 1.0\%$ is possible. The estimated uncertainty of calculated bubble-line densities in the region from

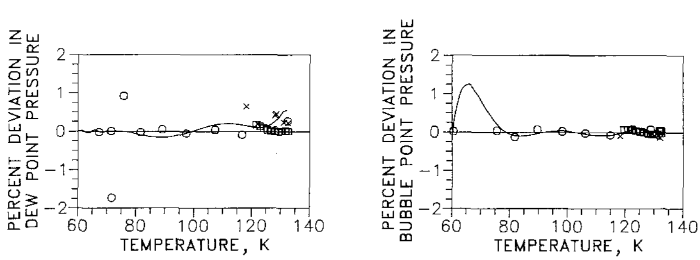

Fig. 2. Comparisons of dew- and bubble-point pressures from Eq. (1) to data from the sources listed in Table II. (□) Rainwater and Van Poolen (this work); (○) Blanke [4]; (——) Blanke and Weiss [21].

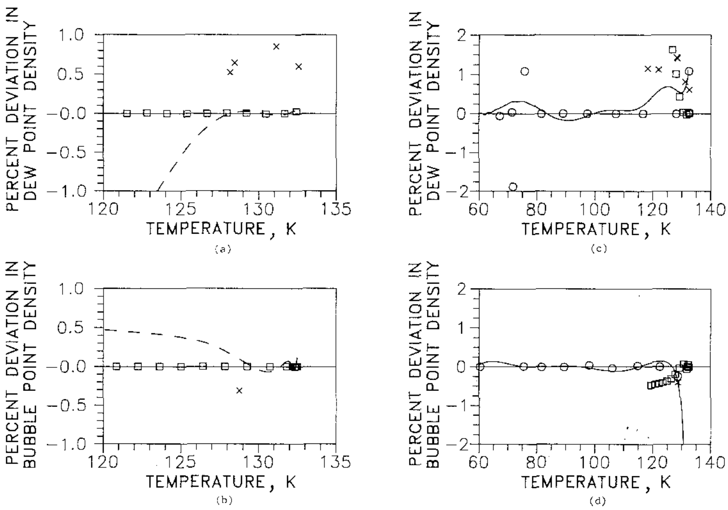

Fig. 3. Comparisons of dew- and bubble-point densities from Eqs. (2) and (3) to data from the sources listed in Table II. (a) Dew point densities from Eq. (2); (b) bubble-point densities from Eq. (2); (c) dew-point densities from Eq. (3); (d) bubble-point densities from Eq. (3). (□) Rainwater and Van Poolen (this work); (○) Blanke [4]; (×) Michels et al. [19]; (——) Blanke and Weiss [21]; (–––) wide-range model, Eq. (3) (this work).

110 K to the maxcondentherm is $\pm 0.5\%$. Calculated densities from Eq. (2) are within $\pm 0.05\%$ of the predicted values from Rainwater and Van Poolen (this work), although the uncertainty of experimental data in this range is generally $\pm 1\%$.

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