Vapor-Liquid Equilibrium Data for Nitrogen–Argon–Oxygen Mixtures

Evaluation and Correlation

IBRAHIM M. ELSHAYAL and BENJAMIN C.-Y. LU
Department of Chemical Engineering, University of Ottawa, Ottawa, Ont., Canada

Vapor-liquid equilibrium data available in the literature for binary and ternary mixtures of nitrogen, argon, and oxygen were tested and screened over the range of temperature from 90° to 120° K. Activity coefficients for the consistent isothermal binary data were correlated by means of the Redlich-Kister equation. The binary constants were successfully employed for predicting the ternary data, without including any ternary constants. Good agreement was obtained between the predicted and the experimental data of Wilson and of Narinskii.

In the low temperature separation of air constituents, vapor-liquid equilibria for mixtures of nitrogen, argon, and oxygen play an important role in the design of the fractionation columns. Although equilibrium data for the binary and the ternary systems have been previously investigated experimentally, the agreement between the numerous set of data is not always good. Latimer (*11*) in 1957, correlated the liquid activity coefficient data by means of the regular solution equations over the pressure range from 0.2 to 20 atm, using published binary and ternary experimental values together with the plant performance data. Wilson *et al.* (*19*) in 1964 made a literature survey for all existing data relating to vapor-liquid equilibrium and enthalpy of the nitrogen–argon–oxygen system up to 1963, and experimentally determined 1962 data points over the pressure range from 1 to 26 atm. The liquid activity coefficient data calculated from the experimental data were correlated by means of the Van Laar equation.

Since the publication of Wilson's data, additional experimental investigations have been reported in the literature. In this investigation, binary vapor-liquid equilibrium data compiled from different sources over the temperature range from 90° to 120° K, were first tested for their consistency, then correlated by means of the Redlich-Kister equation. To avoid the uncertainty due to the temperature effect on liquid activity coefficients, only isothermal data were tested for thermodynamic consistency. The binary constants obtained in this manner were then used to evaluate the ternary liquid activity coefficients for the purpose of determining whether ternary constants are required in the correlation.

EVALUATION OF LIQUID ACTIVITY COEFFICIENTS

In the thermodynamic treatment of the data, the constant-pressure constant-temperature liquid activity coefficient is defined by

$$\gamma_i(P^0, T, x) = \frac{f_{iL}(P, T, x)}{x_i f^0_{iL}(P^0, T)} \exp \int_P^{P^0} \frac{\bar{V}_{iL}}{RT}\, dP \qquad (1)$$

and

$$\gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 1 \qquad (2)$$

In Equation 1, $f_{iL}(P, T, x)$ represents the fugacity of component i in the liquid mixture at system temperature, T, and pressure, P, and $f^0_{iL}(P^0, T)$ represents the fugacity of pure liquid i at the system temperature, T, and the reference pressure P^0. In this investigation, P^0 was arbitrarily taken to be 500 psia, which is above the highest saturation pressure encountered in this work, hence the hypothetical liquid state was avoided. The exponential term represents the pressure correction of γ from P to P^0. The fugacities and the partial molal volumes were obtained from the Redlich-Kwong equation of state by means of a modified procedure (*3*). In the equation

$$P = \frac{RT}{v - b} - \frac{a}{T^{0.5} v(v + b)} \qquad (3)$$

the parameters Ω_a and Ω_b, which are related to the quantities a and b as follows:

$$a = \Omega_a R^2 Tc^{2.5} / Pc \qquad (4)$$

$$b = \Omega_b RTc / Pc \qquad (5)$$

were considered temperature-dependent. The parameters were evaluated using molal volumes and vapor pressures of pure saturated liquids. This modification has been recently presented (*3*). Values of Ω_a and Ω_b used in this work are listed in Table I. The mixing rules employed in this investigation are identical to those reported earlier (*3*). Values of the binary interaction constant k_{ij}, which represents the deviation from the geometric mean of the critical temperatures as defined by Chueh and Prausnitz (*5*), were obtained from the vapor-liquid equilibrium data of the binary systems and are listed in Table II. These values were used in the mixing rules.

CONSISTENCY TEST

Thermodynamic consistencies of binary isothermal data were tested by means of the Redlich-Kister relationship

$$\int_{x_1 = 0}^{x_1 = 1} \ln \frac{\gamma_1}{\gamma_2}\, dx_1 = 0 \qquad (6)$$

Table I. Values of Redlich-Kwong Parameters

Temp, °K	N_2		A		O_2	
	Ω_a	Ω_b	Ω_a	Ω_b	Ω_a	Ω_b
90.5	0.42325	0.08607	0.40582	0.08702	0.41029	0.08653
100	0.42088	0.08457	0.41063	0.08634	0.41481	0.08609
110	0.41656	0.08279	0.41399	0.08560	0.41694	0.08530
120	0.40826	0.08026	0.41399	0.08426	0.41692	0.08419

in which γ values were those obtained from Equation 1 at constant T and P^0.

For ternary isothermal data, the method proposed by Chang and Lu (*4*) was employed. A brief description of the method is presented below.

At constant temperature and pressure, the Gibbs-Duhem equation is:

$$\sum_{i=1}^{n} x_i d \ln \gamma_i = 0 \tag{7}$$

Integrating from point a to its adjacent point b by the trapezoidal rule gives

$$\sum_{i=1}^{n} (x_{ia} + x_{ib})(\ln \gamma_{ib} - \ln \gamma_{ia}) = 0 \tag{8}$$

The assumption involved here is that all the ln γ *vs.* x curves can be approximated by segments of straight lines connecting the points. This approach is identical to that employed by Li and Lu (*12*) and by McDermott and Ellis (*13*). At equilibrium

$$\hat{f}_{iL} = \hat{f}_{iV}$$

and in the vapor phase

$$\hat{f}_{iV} = y_i \phi_i P$$

Hence

$$\gamma_i(P^0, T, x) = \frac{y_i \phi_i P}{x_i f^0_{iL}} \exp \int_P^{P^0} \frac{\bar{V}_{iL}}{RT} dP \tag{11}$$

Substituting Equation 11 into Equation 8 gives

$$\sum_{i=1}^{n} (x_{ib} + x_{ia}) \ln \frac{K_{ib}}{K_{ia}} = \sum_{i=1}^{n} (x_{ib} + x_{ia}) \ln \frac{\phi_{ia} P_a}{\phi_{ib} P_b} + \sum_{i=1}^{n} (x_{ib} + x_{ia}) \int_{P_a}^{P_b} \frac{\bar{V}_{iL}}{RT} dP \tag{12}$$

in which $K_i = y_i/x_i$. The left-hand side of Equation 12 contains only the experimental equilibrium data while the right-hand side contains the quantities which can be evaluated from the Redlich-Kwong equation of state as modified above. To make a test conclusive, maximum experimental error bounds must be established. For isothermal data, the overall deviation resulting from experimental errors of the pair tested may be obtained by rearranging Equation 12 as follows:

$$\Delta = \sum_{i=1}^{n} (x_{ib} + x_{ia}) \left[\ln \frac{K_{ib}}{K_{ia}} - \ln \frac{\phi_{ia} P_a}{\phi_{ib} P_b} - \int_{P_a}^{P_b} \frac{\bar{V}_{iL}}{RT} dP \right] \tag{13}$$

Differentiating Equation 13 and replacing dP, dT, and dx by the measuring errors, $E(P)$, $E(T)$, and $E(x)$, respectively, we find the maximum experimental error bounds are established as follows:

$$|D|_{\max} = \sum_{i=1}^{n} (x_{ib} + x_{ia}) \left[\left(\frac{1}{y_{ib}} + \frac{1}{y_{ia}} + \frac{1}{x_{ib}} + \frac{1}{x_{ia}} \right) + 2 \left| \left(\ln \frac{K_{ib}}{K_{ia}} - \ln \frac{\phi_{ia} P_a}{\phi_{ib} P_b} - \int_{P_a}^{P_b} \frac{\bar{V}_{iL}}{RT} dP \right) \right| \right] E(x) + \sum_{i=1}^{n} (x_{ib} + x_{ia}) \left(\frac{1}{P_a} + \frac{1}{P_b} + \left| \frac{\partial}{\partial P} \int_{P_a}^{P_b} \frac{\bar{V}_{iL}\, dP}{RT} \right| \right) E(P) + \sum_{i=1}^{n} (x_{ib} + x_{ia}) \left| \left(\frac{\partial}{\partial T} \int_{P_a}^{P_b} \frac{\bar{V}_{iL}\, dP}{RT} \right) \right| E(T) \tag{14}$$

where

$E(x)$ = error in composition x or y measurement
$E(P)$ = error in pressure measurement
$E(T)$ = error in temperature measurement

Experimental data which are not widely separated are arranged along any arbitrary path and tested in pairs by means of Equations 13 and 14. Each experimental point appears twice in the test, with the exceptions of the first and the last points of the chosen path. An experimental point is considered inconsistent if Δ is greater than $|D|_{\max}$. In doing so, a point-by-point evaluation of the data is achieved.

NITROGEN-ARGON MIXTURES

Most of the equilibrium data reported in the literature for the binary system nitrogen-argon were restricted to the low temperature region. Since the publication of Wilson's data, additional experimental values were reported by Narinskii (*15*) and by Thorpe (*18*). A static method was used by Thorpe to determine vapor pressures and compositions of this system at pressures up to 10 atm. Unfortunately, isothermal data interpolated from his results did not cover the complete concentration range. On the

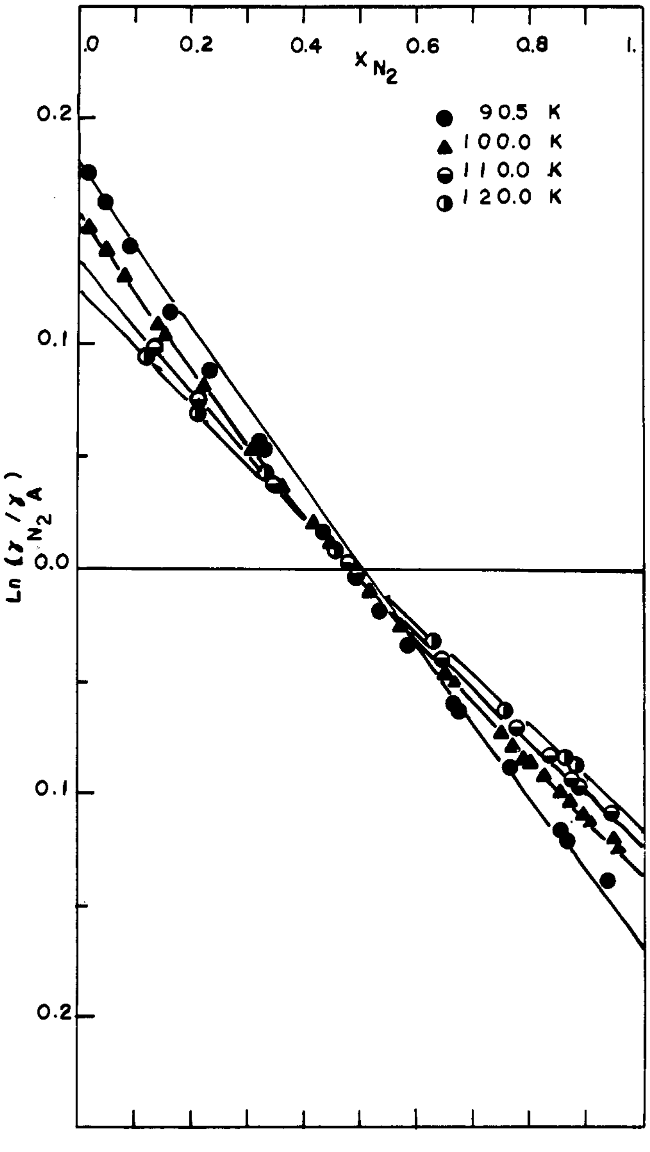

Figure 1. Area test of Narinskii's data for the nitrogen–argon system

Table II. Values of Binary Redlich-Kister Constants

(Ref. pressure = 500 psia)

System	T, °K	B_{ij}	C_{ij}	ln γ_a^∞	ln γ_b^∞	Ref.
Nitrogen-argon	90.5	0.1655	−0.0144	0.1829	0.1541	(*15*)
(k_{12} = 0.0)	100.0	0.1459	−0.0155	0.1574	0.1344	
	110.0	0.1295	−0.0080	0.1375	0.1215	
	120.0	0.1266	−0.0009	0.1275	0.1257	
Argon-oxygen	90.5	0.1878	−0.0027	0.1905	0.1851	(*14*)
(k_{23} = 0.016)	100.0	0.1681	−0.0027	0.1708	0.1654	
	110.0	0.1385	−0.0026	0.1411	0.1359	
	120.0	0.1139	−0.0025	0.1164	0.1114	
Nitrogen-oxygen	90.5	0.2267	0.0198	0.2069	0.2965	(*8*)
(k_{13} = 0.001)	99.94	0.1988	0.0155	0.1833	0.2143	
	110.05	0.1787	0.0113	0.1674	0.1900	
	119.92	0.1715	0.0046	0.1669	0.1761	

other hand, the experimental results of Narinskii were reported over the complete concentration range at four isothermal conditions, namely 90.5°, 100°, 110°, and 120° K. Liquid activity coefficient values obtained from Equation 1 for Narinskii's data satisfy the area test as shown in Figure 1.

ARGON-OXYGEN MIXTURES

For the binary system argon-oxygen, available literature data include those of Bourbo and Ishkin (*1*), Sagenkahn and Fink (*17*), Clark *et al.* (*6*), Fastovskii and Petrovskii (*9, 10*), Narinskii (*14*), and Burn and Din (*2*). Results

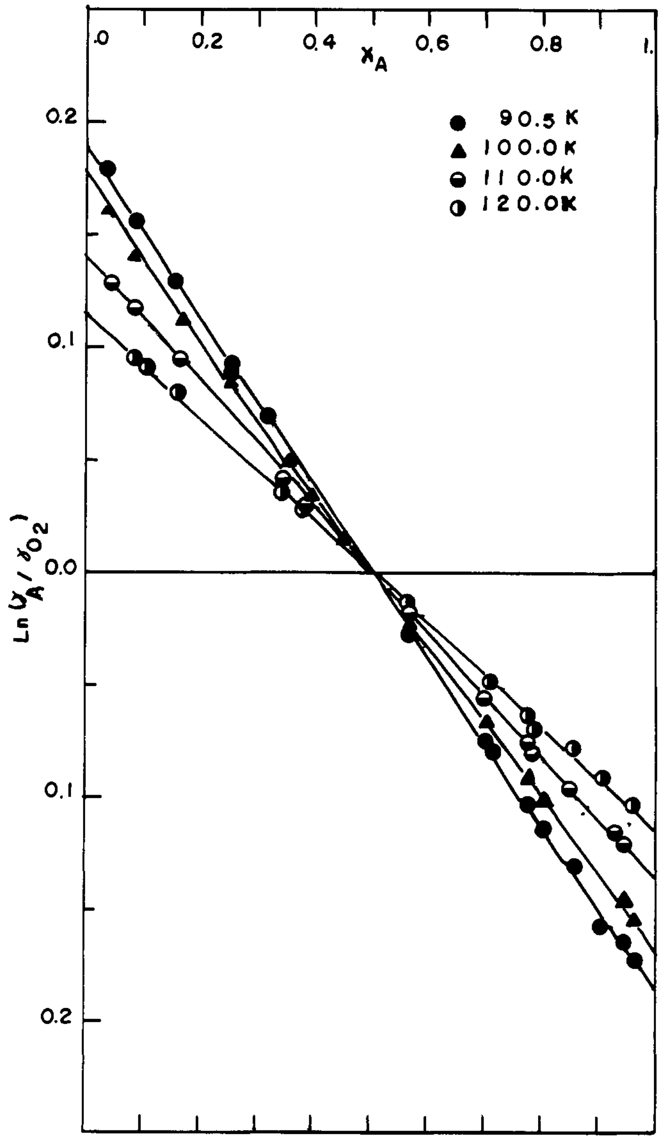

Figure 2. Area test of Narinskii's data for the argon-oxygen system

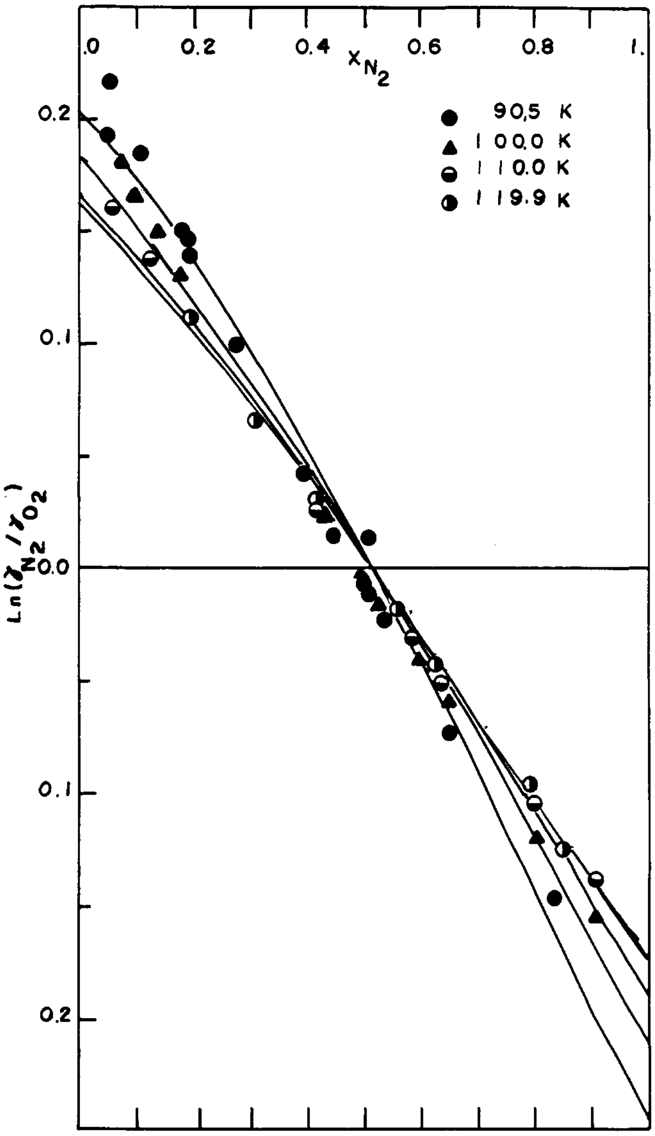

Figure 3. Area test of the data of Dodge and Dunbar for the nitrogen-oxygen system

of the three investigations (*2*, *6*, *14*) which cover the complete concentration range were tested for their thermodynamic consistency by means of the area-test method. The results of the test indicate that the data of Clark *et al.* (*6*) are inconsistent. Burn and Din (*2*) studied this system over the complete concentration range and over a pressure range of 1 to 10 atm using a static method. They stated that their data agreed well with the isothermal data of Narinskii (*14*) who reported the data at 90.5°, 100°, 110°, and 120° K. The results of the area test as shown in Figure 2 indicate that the data of Narinskii are thermodynamically consistent.

NITROGEN–OXYGEN MIXTURES

In the temperature range of this investigation, literature data for the binary system nitrogen–oxygen include those of Dodge and Dunbar (*8*) and Din (*7*).

Results of the area test indicate that the isothermal data of Din are thermodynamically inconsistent, while the isothermal data of Dodge and Dunbar satisfy the test. The area test of the data of Dodge and Dunbar (*8*) is shown in Figure 3.

CORRELATION OF BINARY LIQUID ACTIVITY COEFFICIENTS

The thermodynamically consistent liquid activity coefficients for the three binary systems were successfully correlated using the least-squares method by a two-constant Redlich-Kister equation as follows:

$$\ln \gamma_i = x_j^2 [B_{ij} + C_{ij}(3\, x_i - x_j)] \tag{15}$$

and

$$\ln \gamma_j = x_i^2 [B_{ij} + C_{ij}(x_i - 3\, x_j)] \tag{16}$$

Values of B_{ij} and C_{ij} obtained at four temperatures for the three binary systems are listed in Table II. Values of ln γ at infinite dilutions are also listed in this table.

The calculated γ values agree well with the experimental data. A comparison at 100° K for the three binary systems is given in Tables III–V.

Table III. Comparison of Calculated and Experimental γ Values for System Nitrogen–Argon at 100° K

		γ_{N_2}		γ_A	
P_{psia}	x_{N_2}	Exptl (*15*)	Calcd	Exptl (*15*)	Calcd
48.56	0.0195	1.0001	1.0001	1.1635	1.1624
50.90	0.0480	1.0005	1.0004	1.1518	1.1510
53.07	0.0813	1.0012	1.0012	1.1389	1.1385
57.40	0.1400	1.0035	1.0034	1.1182	1.1181
58.58	0.1565	1.0044	1.0043	1.1128	1.1128
62.87	0.2222	1.0086	1.0084	1.0930	1.0931
68.98	0.3092	1.0161	1.0160	1.0706	1.0707
72.12	0.3618	1.0217	1.0217	1.0590	1.0590
75.84	0.4142	1.0281	1.0281	1.0487	1.0486
77.79	0.4421	1.0318	1.0318	1.0437	1.0436
82.27	0.5169	1.0426	1.0427	1.0319	1.0317
85.45	0.5703	1.0512	1.0514	1.0248	1.0245
90.69	0.6483	1.0650	1.0653	1.0163	1.0159
91.92	0.6597	1.0672	1.0675	1.0152	1.0148
92.27	0.7485	1.0849	1.0852	1.0082	1.0078
98.28	0.7691	1.0893	1.0896	1.0069	1.0065
99.45	0.7888	1.0936	1.0938	1.0057	1.0054
100.20	0.7982	1.0957	1.0959	1.0052	1.0049
101.91	0.8230	1.1012	1.1014	1.0041	1.0038
103.47	0.8514	1.1078	1.1078	1.0029	1.0026
104.78	0.8685	1.1119	1.1118	1.0023	1.0020
105.93	0.8903	1.1171	1.1169	1.0016	1.0014
106.83	0.9001	1.1195	1.1192	1.0014	1.0012
106.69	0.9444	1.1307	1.1300	1.0006	1.0004
109.56	0.9470	1.1313	1.1306	1.0005	1.0003

Comparison with Binary Data of Wilson. Wilson studied the three binary systems at isobaric conditions and graphically reported ln γ values at 20° R intervals. The binary constants obtained in this investigation were used to obtain the ln γ curves at constant temperatures which were then compared with the isobaric data reported by Wilson over the appropriate intervals. The reference pressure used in this comparison is identical to that employed by Wilson. The agreement obtained appears to be as satisfactory as Wilson's own correlation (*19*). The comparisons made at the interval between 100° and 110° K for the three binary systems are shown in Figures 4–6 as examples.

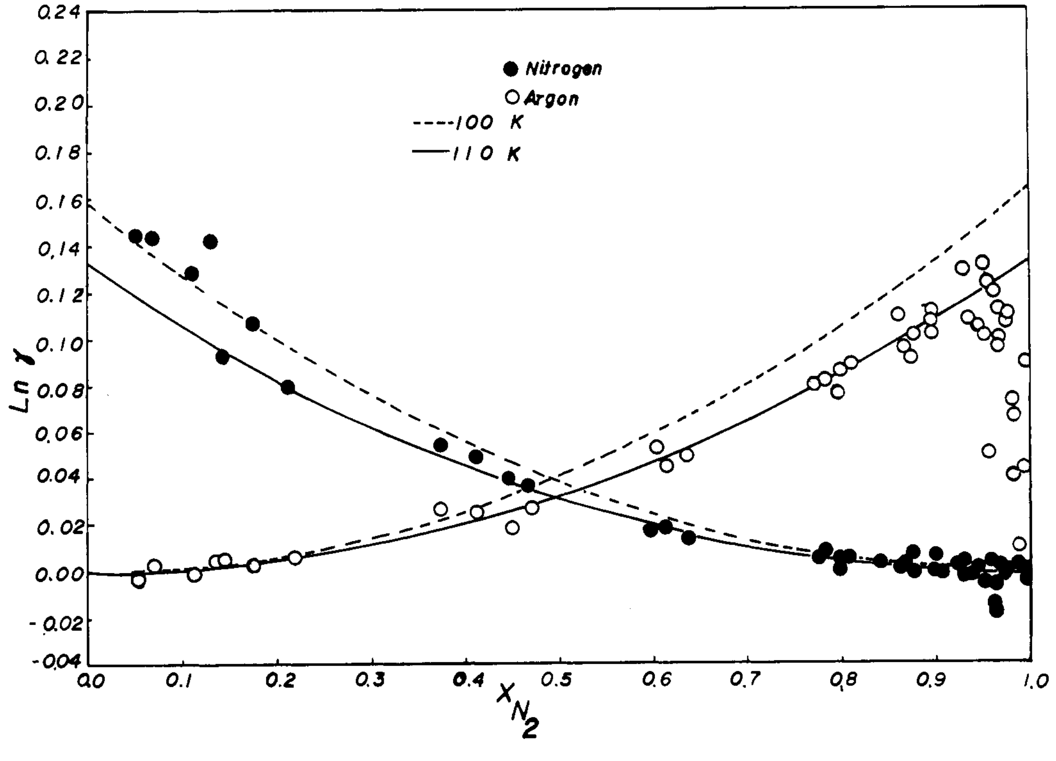

Figure 4. Comparison of Wilson's experimental γ and the calculated γ values for the nitrogen–argon system at the interval between 100° and 110° K

Experimental ··· — Calculated

Table IV. Comparison of Experimental and Calculated Values of γ for System Argon–Oxygen at 100° K

		γ_A		γ_{O_2}	
P_{psia}	x_A	Exptl (*14*)	Calcd	Calcd	Exptl (*14*)
37.84	0.0323	1.1732	1.1730	1.0002	1.0002
38.20	0.0855	1.1527	1.1526	1.0013	1.0013
39.57	0.1698	1.1235	1.1235	1.0050	1.0050
40.72	0.2519	1.0986	1.0986	1.0111	1.0111
42.00	0.3505	1.0729	1.0730	1.0214	1.0214
42.46	0.3942	1.0630	1.0630	1.0271	1.0271
43.10	0.4506	1.0514	1.0514	1.0354	1.0354
44.22	0.5684	1.0312	1.0312	1.0564	1.0565
45.27	0.6985	1.0150	1.0150	1.0857	1.0858
45.81	0.7736	1.0084	1.0084	1.1056	1.1057
46.03	0.8020	1.0064	1.0064	1.1137	1.1138
46.52	0.9048	1.0015	1.0015	1.1460	1.1460
46.74	0.9429	1.0005	1.0005	1.1592	1.1591
46.82	0.9604	1.0003	1.0003	1.1654	1.1653

Table V. Comparison of Calculated and Experimental γ Values for System Oxygen–Nitrogen at 99.94° K

		γ_{O_2}		γ_{N_2}	
P_{psia}	x_{O_2}	Exptl (*8*)	Calcd	Exptl (*8*)	Calcd
40.11	0.9500	1.2110	1.2099	1.0006	1.0006
42.66	0.9299	1.1997	1.1990	1.0012	1.0012
44.41	0.9005	1.1841	1.1838	1.0025	1.0024
47.85	0.8640	1.1660	1.1661	1.0045	1.0044
50.73	0.8209	1.1464	1.1467	1.0077	1.0075
56.51	0.7488	1.0428	1.0426	1.0593	1.0596
69.95	0.5752	1.0641	1.0642	1.0403	1.0403
74.11	0.5125	1.0496	1.0495	1.0523	1.0524
82.64	0.4103	1.0307	1.0307	1.0748	1.0753
85.84	0.3624	1.0236	1.0232	1.0866	1.0872
97.58	0.1944	1.0066	1.0062	1.1346	1.1352
105.52	0.0914	1.0016	1.0016	1.1681	1.1688

NITROGEN–ARGON–OXYGEN MIXTURES

Very limited data for the ternary system were available in the literature prior to Wilson's experimental investigation, which includes a total of 1962 data points. Recently, Narinskii (*16*) studied the ternary mixtures by means of a circulation method at temperatures of 90.5°, 100°, 110°, and 120° K.

In this investigation, the binary constants obtained at isothermal conditions were used to evaluate the ternary liquid activity coefficients by means of the following expressions:

$$\begin{aligned}\ln \gamma_1 = {} & B_{12}x_2(1 - x_1) + C_{12}x_2(2\ x_1 - x_2 - 2\ x_1^2 + 2\ x_1x_2) - \\ & B_{23}x_2x_3 - 2\ C_{23}x_2x_3(x_2 - x_3) + \\ & B_{31}x_3(1 - x_1) + C_{31}x_3(x_3 - 2\ x_1x_3 + 2\ x_1^2 - 2\ x_1)\end{aligned} \tag{17}$$

$$\begin{aligned}\ln \gamma_2 = {} & B_{12}x_1(1 - x_2) + C_{12}x_1(x_1 - 2\ x_2 - 2\ x_1x_2 + 2\ x_2^2) + \\ & B_{23}x_3(1 - x_2) + C_{23}x_3(2\ x_2 - x_3 - 2\ x_2^2 + 2\ x_2x_3) - \\ & B_{13}x_1x_3 - 2\ C_{31}x_1x_3(x_3 - x_1)\end{aligned} \tag{18}$$

and

$$\begin{aligned}\ln \gamma_3 = {} & -B_{12}x_1x_2 - 2\ C_{12}x_1x_2(x_1 - x_2) + \\ & B_{23}x_2(1 - x_3) + C_{23}x_2(x_2 - 2\ x_3 - 2\ x_2x_3 + 2\ x_3^2) + \\ & B_{31}x_1(1 - x_3) + C_{31}x_1(2\ x_3 - x_1 - 2\ x_3^2 + 2\ x_1x_3)\end{aligned} \tag{19}$$

In these expressions the ternary constants were neglected and only binary constants were involved.

The thermodynamic consistency of the isothermal data of Narinskii was tested by means of the test method described above. The calculated γ values obtained were then compared with the consistent data of Narinskii. The comparison made at 100° K is given in Table VI as an example. A summary of the comparison is given in Table VII. The average absolute deviation is generally less than 2%.

The calculated γ values obtained from Equations 17–19 were then compared with the consistent data of Wilson. Although Wilson studied the ternary system at isobaric conditions, it was possible to select a sufficient number

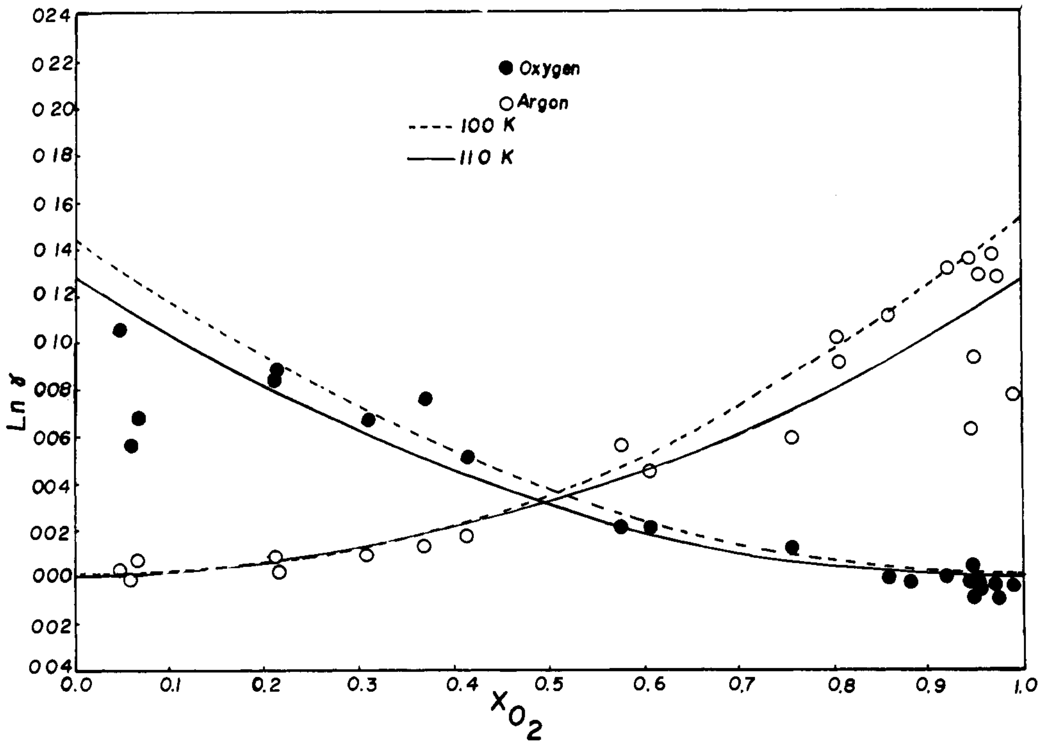

Figure 5. Comparison of Wilson's experimental γ and the calculated γ values for the argon–oxygen system at the interval between 100° and 110° K

Experimental --- — Calculated

Table VI. Comparison of Calculated and Experimental γ Values for System Nitrogen–Argon–Oxygen at 100.0° K

			γ_A		γ_{O_2}		γ_{N_2}	
P_{psia}	x_A	x_{O_2}	Exptl (*16*)	Calcd	Exptl (*16*)	Calcd	Exptl (*16*)	Calcd
104.34	0.1073	0.0393	1.1201	1.1713	1.1582	1.1317	1.0025	1.0039
97.77	0.1666	0.0929	1.0991	1.1355	1.1342	1.1056	1.0075	1.0112
90.44	0.2627	0.0896	1.0784	1.1007	1.1259	1.0977	1.0145	1.0220
92.86	0.2315	0.0865	1.0854	1.1118	1.1295	1.1008	1.0117	1.0178
66.97	0.5019	0.1711	1.0323	1.0362	1.0974	1.0805	1.0577	1.0752
55.64	0.6869	0.1130	1.0132	1.0134	1.1176	1.1078	1.0926	1.1151
51.36	0.6757	0.2045	1.0136	1.0143	1.0997	1.0932	1.1085	1.1259
46.73	0.7654	0.1683	1.0074	1.0076	1.1154	1.1112	1.1299	1.1472
79.37	0.3020	0.2086	1.0622	1.0778	1.0925	1.0686	1.0304	1.0399
68.48	0.4601	0.2058	1.0370	1.0425	1.0896	1.0722	1.0550	1.0705
87.03	0.1417	0.2896	1.0894	1.1221	1.0838	1.0595	1.0233	1.0267
82.61	0.1598	0.3326	1.0843	1.1130	1.0725	1.0501	1.0309	1.0343
78.76	0.1681	0.3859	1.0820	1.1079	1.0608	1.0409	1.0403	1.0429
70.95	0.3368	0.3105	1.0535	1.0650	1.0692	1.0512	1.0508	1.0600
60.22	0.4806	0.3008	1.0338	1.0380	1.0714	1.0599	1.0772	1.0897
50.70	0.5414	0.3750	1.0299	1.0315	1.0626	1.0578	1.1116	1.1181
51.58	0.4617	0.4501	1.0420	1.0444	1.0478	1.0431	1.1107	1.1118
58.62	0.3672	0.4566	1.0529	1.0597	1.0438	1.0351	1.0890	1.0909
71.45	0.1234	0.5474	1.0944	1.1197	1.0342	1.0212	1.0681	1.0628
61.25	0.1224	0.6964	1.1086	1.1250	1.0149	1.0090	1.1115	1.0917
57.86	0.0955	0.7759	1.1246	1.1375	1.0081	1.0048	1.1136	1.1047

Table VII. Summary of Comparison of Calculated and Experimental γ Values for Ternary System

Source	Temp, °K	No. of exptl points	Average absolute deviation, %		
			γ_A	γ_{O_2}	γ_{N_2}
Narinskii (*16*)	90.5	21	1.14	2.04	1.24
	100	21	1.45	1.42	0.95
	110	27	1.25	1.26	0.97
	120	25	1.30	1.23	0.83
Wilson (*19*)	90.5	13	0.73	0.96	0.82
	100	24	0.30	0.39	0.41
	110	41	0.30	0.40	0.59
	120	22	1.09	1.05	0.43

of data points at constant temperatures. These values were tested for consistency and screened. In this comparison, γ values of Wilson's data were obtained at the reference pressure of this investigation. A summary of the comparison is also given in Table VII. The average absolute deviation is generally less than 1%.

CONCLUSIONS

In conclusion, it may be stated that available vapor-liquid equilibrium data for binary and ternary mixtures of nitrogen, argon, and oxygen in the temperature range from 90° to 120° K have been tested and screened. The binary Redlich-Kister constants obtained from consistent isothermal data at four temperatures have been successfully

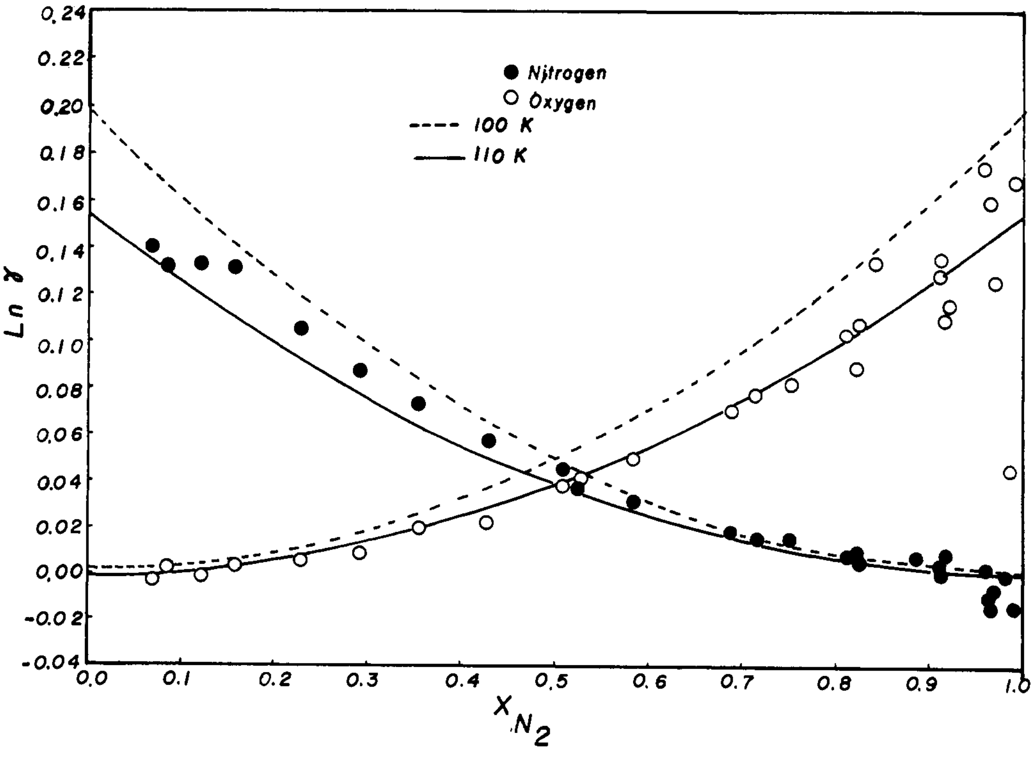

Figure 6. Comparison of Wilson's experimental γ and the calculated γ values for the nitrogen–oxygen system at the interval between 100° and 110° K

Experimental --- — Calculated

employed for predicting the ternary data without including any ternary constants. The calculated ternary γ values agree well with the data of Narinskii and of Wilson.

ACKNOWLEDGMENT

The authors wish to thank Shinn-Der Chang for his assistance.

NOMENCLATURE

a, b = constants in the Redlich-Kwong equation of state
B, C = constants in the Redlich-Kister equation
f = fugacity, psia
k = interaction constant
P = pressure, psia
R = gas constant
T = absolute temperature, ° K
v = molal volume, cu ft/lb mole
x = liquid phase composition
y = vapor phase composition
γ = activity coefficient
ϕ = fugacity coefficient
Ω_a, Ω_b = parameters in the Redlich-Kwong equation of state

Subscripts

c = critical property
i, j = components of mixture
ij = interaction property
L = liquid phase
V = vapor phase
a, b = first and second components respectively

Superscripts

^{0} = reference state
$\overline{\ }$ = partial molar property
$\hat{\ }$ = solution property

LITERATURE CITED

(1) Bourbo, P., Ishkin, I., *Physica*, **3**, 1067 (1936).
(2) Burn, I., Din, F., *Trans. Faraday Soc.*, **58**, 1341 (1962).
(3) Chang, S.-D., Lu, B. C.-Y., *Can. J. Chem. Eng.*, **48**, 261 (1970).
(4) Chang, S.-D., Lu, B. C.-Y., The Proceeding of International Symposium on Distillation, Brighton, England, Sept. 1969.
(5) Chueh, P. L., Prausnitz, J. M., *A.I.Ch.E. J.*, **13**, 1099 (1967).
(6) Clark, A. M., Din, F., Robb, *J. Proc. Roy. Soc.* (London), **221A**, 517 (1954).
(7) Din, F., *Trans. Faraday Soc.*, **56**, 668 (1960).
(8) Dodge, B. F., Dunbar, A. K., *J. Amer. Chem. Soc.*, **49**, 591 (1927).
(9) Fastovskii, V. G., Petrovskii, V. Yu., *Zh. Fiz. Khim.*, **29**, 1311 (1955).
(10) Fastovskii, V. G., Petrovskii, V. Yu., *ibid.*, **30**, 76 (1956).
(11) Latimir, R. E., *AIChE J.* **3**, 75 (1957).
(12) Li, J. C. M., Lu, B. C.-Y., *Can. J. Chem. Eng.*, **37**, 117 (1959).
(13) McDermott, C., Ellis, S. R. M., *Chem. Eng. Sci.*, **20**, 293 (1965).
(14) Narinskii, G. B., *Kislorod*, **10** (3), 9 (1957).
(15) Narinskii, G. B., *Russ. J. Phys. Chem.*, **40** (9), 1093 (1966).
(16) Narinskii, *ibid.*, **43** (2), 219 (1969).
(17) Sagenkahn, M. L., Fink, H. L., *O.S.R.D.*, 4493, Pennsylvania State College (1944).
(18) Thorpe, P. L., *Trans. Faraday Soc.*, **64**, 2273 (1968).
(19) Wilson, G. M., Silverberg, P. M., Zellener, M. G., Technical Documentary Report No. APL-TDR-64-64, April 1964, AF Aero Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, U. S. A. [See also Wilson, G. M., Advances in cryogenic Engineering Vol. 10, p. 192, (Ed. K. D. Timmerhaus), Plenum Press, New York, (1965).]

RECEIVED for review April 24, 1970. Accepted August 15, 1970. Work supported by the National Research Council of Canada.

Vapor-Pressure Relationships for Hexafluorides

JAMES K. SHOU and CHARLES E. HAMRIN, Jr.[1]
University of Denver, Denver, Colo. 80210

Vapor pressure data for nine hexafluorides were fitted to the Frost-Kalkwarf equation, $\log P = A + B/T + C \log T + D(P/T^2)$. A reduced form of this equation was developed which requires the critical temperature, critical pressure, and Pitzer's ω factor for application. Sublimation pressure data for 13 hexafluorides were fitted to a two constant equation, $\log P' = A' + B'/T$.

Several investigators have recently compared different vapor pressure equations to test their reliability over wide ranges of temperature and pressure (*15, 20, 27*). The Frost-Kalkwarf equation (*8*) as modified by Reynes and Thodos (*23, 24*) was found to be the best equation over the pressure range from 10 torr to the critical pressure (*15*). They presented this equation in the following form:

$$\log P_R = \beta\left(\frac{1}{T_R} - 1\right) + \left(\frac{9}{5}\beta + \frac{8}{3}\right)\log T_R + 0.1832\left(\frac{P_R}{T_R^2} - 1\right) \qquad (1)$$

which requires knowledge of the critical temperature, the critical pressure, and the constant β.

Since the Frost-Kalkwarf equation has been found to represent vapor pressure data very well, it was chosen for this study with the hexafluorides. The hexafluorides were selected as a group because of their molecular symmetry and their increasing industrial importance.

DATA FOR HEXAFLUORIDES

An extensive search of the literature was performed to locate vapor pressure data for the hexafluorides. Sublimation pressure data were also obtained. Primary data sources are shown in Table I as well as values of the critical properties and the triple points. The critical proper-

---

[1] Present address, Department of Chemical Engineering, University of Kentucky, Lexington, Ky. 40506. To whom correspondence should be addressed.