Vapor-liquid Equilibria of Nitrogen-argon-oxygen Mixtures

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The equations and graphs presented here for the vapor-liquid equilibrium of the nitrogen-argon-oxygen low-temperature system are based on published binary and ternary experimental data involving mixtures of nitrogen, argon, and oxygen, and on careful thermodynamic study over a period of years of accurate plant-performance data on tall, large air-rectifying columns operating near the minimum reflux ratios. The plants have achieved separations that are impossible according to some of the published equilibrium data, and thus the plant data have made a major contribution toward the preparation of this paper.

The vapor-liquid equilibrium of the nitrogen-argon-oxygen low-temperature system is described in this paper over the range of pressure from 0.2 to 20 atm. by the simple equations for "regular" solutions and by simple equations for vapor pressures and for the ratio of fugacity coefficients. For convenience these equations are plotted on a large number of graphs, some of which are included in this paper and all of which are available.*

VAPOR PRESSURES

The vapor pressures of nitrogen-argon-oxygen liquid mixtures are represented by the equation

$$\log_{10} P = a - \frac{b}{T} \qquad (1)$$

in which P is the vapor pressure in atmospheres, T is the absolute temperature in degrees Kelvin, and a and b are functions of the liquid composition. Table 1 shows values of a and b at 10% intervals of composition, from Clark, Din, and Robb (*2*) for argon-oxygen mixtures; from Dodge and Dunbar (*3*) for nitrogen-oxygen mixtures except 100% oxygen; and interpolated from the data of Holst and Hamburger (*4*) for nitrogen-argon mixtures except 100% nitrogen and 100% argon. Figures 1, 2, and 3 show the vapor pressures according to Table 1 for nitrogen-argon, nitrogen-oxygen, and argon-oxygen mixtures, respectively, from 0.2 to 20 atm., as a

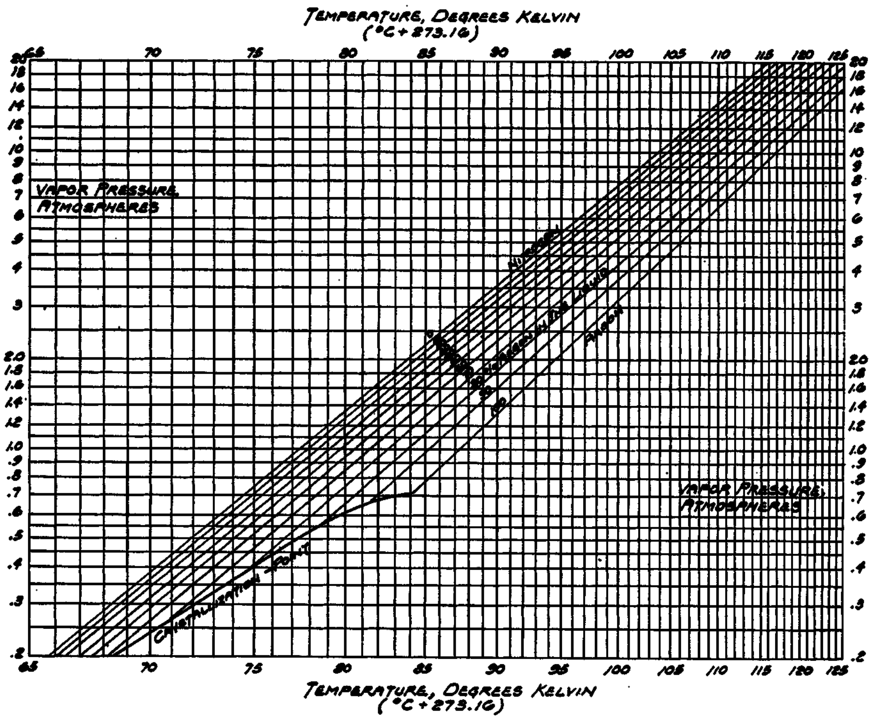

Fig. 1. Vapor pressure of N_2-A liquid mixtures.

TABLE 1

VAPOR PRESSURES OF NITROGEN-ARGON, ARGON-OXYGEN, AND NITROGEN-OXYGEN BINARY LIQUID MIXTURES

$$\log_{10} P_{atm} = a - \frac{b}{T°\text{K.}} \qquad T°\text{K.} = \frac{b}{a - \log_{10} P_{atm}}$$

Data of Clark, Din, and Robb for argon-oxygen
Data of Dodge and Dunbar for nitrogen-oxygen, except 100% oxygen
Data of Holst and Hamburger for nitrogen-argon, except 100% nitrogen and 100% argon

% N_2	% O_2	*a*	*b*	% N_2	% A	*a*	*b*	% A	% O_2	*a*	*b*
100	0	3.9335	304.49	100	0	3.9335	304.49	100	0	3.96370	346.000
90	10	3.9051	304.52	90	10	3.9164	305.0	90	10	3.96748	346.709
80	20	3.8818	305.35	80	20	3.9018	306.0	80	20	3.97276	347.782
70	30	3.8626	306.84	70	30	3.8881	307.5	70	30	3.97896	349.107
60	40	3.8493	309.21	60	40	3.8746	309.3	60	40	3.98603	350.661
50	50	3.8418	312.52	50	50	3.8610	311.5	50	50	3.99396	352.439
40	60	3.8444	317.32	40	60	3.8475	313.9	40	60	4.00279	354.445
30	70	3.8585	323.89	30	70	3.8405	317.0	30	70	4.01258	356.689
20	80	3.8915	333.18	20	80	3.8482	322.1	20	80	4.02340	359.189
10	90	3.9541	346.64	10	90	3.8743	330.36	10	90	4.03543	361.985
0	100	4.0490	365.19	0	100	3.96370	346.000	0	100	4.04898	365.186

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*Figures 13 to 32, and 34 to 49 are omitted from this paper owing to lack of space. The complete set of diagrams, Figures 1 to 49, is available as Document 5032 from the American Documentation Institute, Auxiliary Publications Service, Library of Congress, Washington 25, D.C., at $8.75 for photoprints or $3.00 for 35-mm. microfilm.

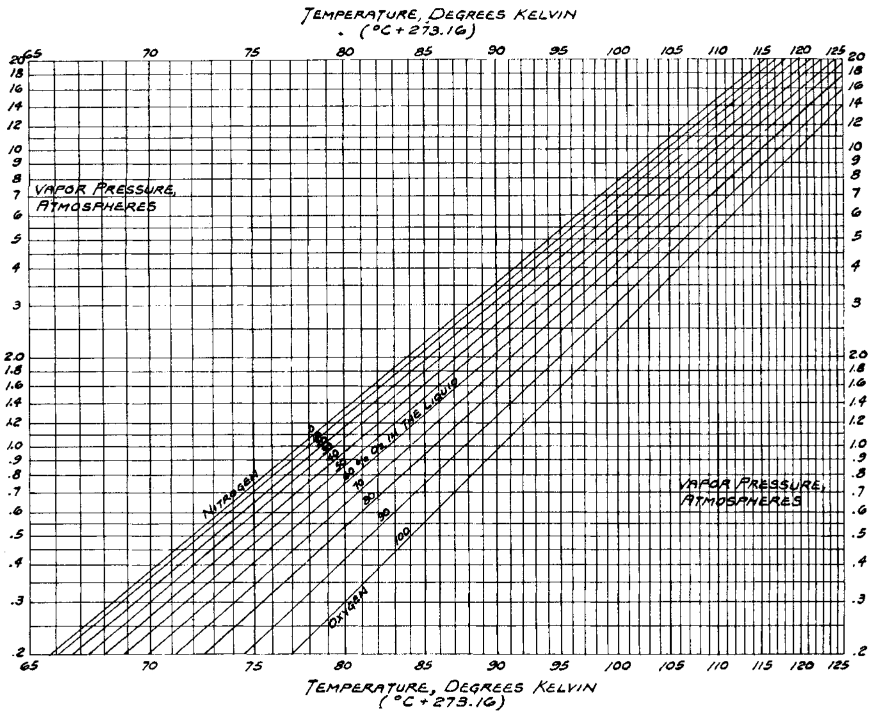

Fig. 2. Vapor pressure of N_2-O_2 liquid mixtures.

function of absolute temperature, with lines at 10 or 20% intervals of liquid composition. The crystallization-point phase boundary is plotted on Figures 1 and 3 from the solid-liquid–equilibrium data reported by Ruhemann, Lichter, and Komarow (*8*).

As a fairly good approximation, straight-line interpolations of the constants *a* and *b* are made in Figure 4 for ternary mixtures from the values for binary mixtures in Table 1. Values of the constants can be read from Figure 4 with sufficient accuracy for most purposes. Table 2 shows the bubble-point temperatures at 1,000 mm. of mercury as measured by Weishaupt (*9*) for forty-one mixtures of nitrogen-argon-oxygen, in comparison with the temperatures computed by use of *a* and *b* constants read from Figure 4. The experimental temperatures have a mean absolute deviation of 0.19°C. and a mean algebraic deviation of 0.07°C. from those computed from Figure 4.

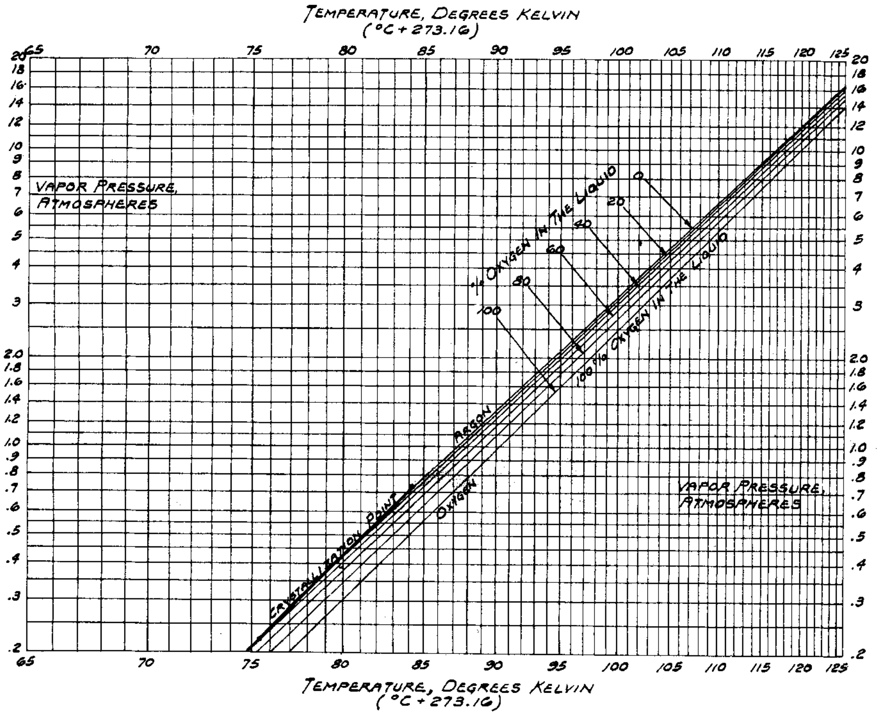

Fig. 3. Vapor pressure of A-O_2 liquid mixtures.

VAPOR-LIQUID EQUILIBRIUM AS A FUNCTION OF TEMPERATURE AND COMPOSITION

Raoult's Law states that the partial pressure of a component *i* in a liquid solution is equal to the vapor pressure of that component times its mole fraction in the liquid:

$$p_i = P_i x_i \tag{2}$$

Dalton's Law states that the partial pressure is also equal to the total pressure times the mole fraction in the vapor:

$$p_i = \pi y_i \tag{3}$$

Combining these two expressions gives

$$p_i = \pi y_i = P_i x_i \tag{4}$$

The relative volatility of component *i* with respect to component *k* can then be written as follows:

$$\alpha_{ik} = \frac{y_i/x_i}{y_k/x_k} = \frac{P_i/\pi}{P_k/\pi} = \frac{P_i}{P_k} \tag{5}$$

The foregoing equations apply only to "ideal" liquid solutions and "ideal" gases (at low pressure). Except at very low pressure, fugacities must be substituted for pressures in these equations, and thus Raoult's and Dalton's laws are converted into the Lewis and Randall equations:

$$f_i = f_{\pi i}{}^0 y_i = f_{Pi}{}^0 x_i e^{v_{Li}(\pi - P_i)/RT} \tag{6}$$

$$\alpha_{ik} = \frac{y_i/x_i}{y_k/x_k}$$

$$= \frac{f_{Pi}{}^0 e^{v_{Li}(\pi - P_i)/RT} / f_{\pi i}{}^0}{f_{Pk}{}^0 e^{v_{Lk}(\pi - P_k)/RT} / f_{\pi k}{}^0} \tag{7}$$

If the liquid solution is not ideal, the liquid-phase activity coefficient γ_i must be inserted into the Raoult's Law and the Lewis and Randall equations. Thus, at low pressures

$$p_i = \gamma_i P_i x_i \tag{8}$$

$$p_i = \pi y_i = \gamma_i P_i x_i \tag{9}$$

$$\alpha_{ik} = \frac{y_i/x_i}{y_k/x_k} = \frac{\gamma_i P_i}{\gamma_k P_k} \tag{10}$$

And at higher pressures, with negligible deviation of the vapor phase from the Lewis and Randall equation assumed,

$$f_i = f_{\pi i}{}^0 y_i$$

$$= \gamma_i f_{Pi}{}^0 x_i e^{v_{Li}(\pi - P_i)/RT} \tag{11}$$

$$\alpha_{ik} = \frac{y_i/x_i}{y_k/x_k}$$

$$= \frac{\gamma_i f_{P_i}{}^0 e^{v_{Li}(\pi - P_i)/RT} / f_{\pi i}{}^0}{\gamma_k f_{P_k}{}^0 e^{v_{Lk}(\pi - P_k)/RT} / f_{\pi k}{}^0} \qquad (12)$$

Further in this paper, evidence is presented to show that nitrogen-oxygen, argon-oxygen, and nitrogen-argon liquid binary mixtures are "regular" solutions (3a), for which the entropy of mixing is the same as for ideal-liquid solutions; that is, the excess entropy of mixing is zero. For a regular binary solution of components i and k, the equations for the liquid-phase activity coefficients are

$$T \log_{10} \gamma_i = c x_k^2 \qquad (13)$$

$$T \log_{10} \gamma_k = c x_i^2 \qquad (14)$$

The constant c is the same for both components and is likely to be independent of the temperature; therefore,

$$T \log_{10} \frac{\gamma_i}{\gamma_k} = c(x_k^2 - x_i^2)$$
$$= c(x_k - x_i)(x_k + x_i)$$
$$= c(x_k - x_i) \qquad (15)$$

For regular binary solutions at a liquid composition of 50% of each component, x_i equals x_k equals 0.50, and γ_i equals γ_k. Thus, for regular binary solutions at 50-50 liquid composition Equation (12) reduces to Equation (7). And for binary regular solutions—if it is known or may be presumed that they are regular solutions—the relative volatility at 50-50 composition can be evaluated as a function of temperature from vapor-pressure data, from data as to density of the pure-component liquids, and from the Hougen and Watson (5) generalized fugacity chart.

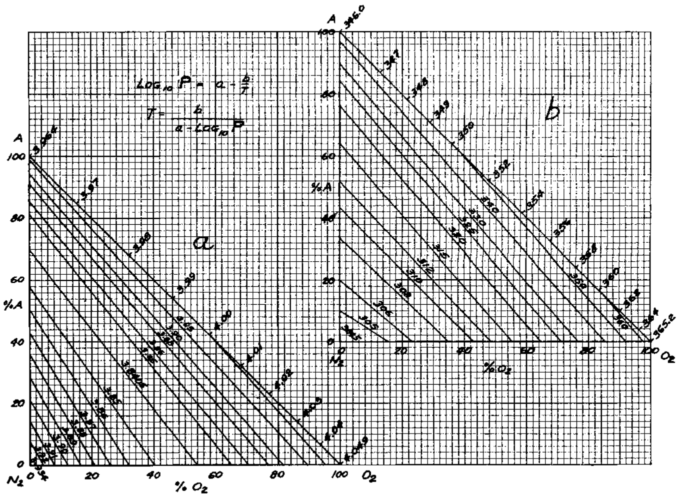

Fig. 4. Constants a and b in the vapor-pressure equation for N_2-A-O_2 liquid mixtures.

Since

$$\log P_i = a - \frac{b}{T} \qquad (1)$$

then

$$\log \alpha_{ik(ideal)} = \log \frac{P_i}{P_k} = a' - \frac{b'}{T} \qquad (16)$$

Likewise, $\log \alpha_{ik(50\text{-}50)}$ can be approximated by the same form of equation:

$$\log \alpha_{ik(50\text{-}50)} = a'' - \frac{b''}{T} \qquad (17)$$

Equation (7) has been evaluated for the three binary 50-50 mixtures at a number of temperatures and pressures, and these values of $\alpha_{ik(50\text{-}50)}$ are accurately represented from 0.2 to 20 atm. in the manner of Equation (17), as follows:

TABLE 2

COMPARISON OF WEISHAUPT EXPERIMENTAL NITROGEN-ARGON-OXYGEN EQUILIBRIUM DATA AT 1,000 MM. HG WITH WEISHAUPT'S EQUATIONS AND THE WRITER'S EQUATIONS

Subscripts: x Weishaupt experimental data, r recommended equations of this paper

						Experimental			Weishaupt equations			Experimental			Weishaupt equations			Writer's equations		
Run	x_O	x_A	x_N	T_x	T_r	y_O	y_A	y_N	y_O	y_A	y_N	α_{NO}	α_{AO}	α_{NA}	α_{NO}	α_{AO}	α_{NA}	α_{NO}	α_{AO}	α_{NA}
8	0.1159	0.1115	0.7726		81.32	0.0331	0.0453	0.9216	0.0385	0.0505	0.9110	4.177	1.422	2.935	3.555	1.362	2.605	3.573	1.456	2.455
9	0.1496	0.1447	0.7057		81.80	0.0531	0.0771	0.8698	0.0524	0.0690	0.8786	3.470	1.501	2.310	3.552	1.362	2.604	3.615	1.449	2.492
10	0.2058	0.1939	0.6003	83.21	82.70	0.0840	0.1214	0.7946	0.0787	0.1011	0.8202	3.25	1.536	2.12	3.577	1.361	2.629	3.611	1.430	2.525
12	0.2047	0.1130	0.6823	82.27	82.08	0.0726	0.0655	0.8619	0.0729	0.0558	0.8713	3.56	1.633	2.18	3.590	1.388	2.590	3.622	1.469	2.466
13	0.3403	0.1317	0.5280	83.71	83.56	0.1401	0.0744	0.7855	0.1386	0.0765	0.7849	3.61	1.371	2.63	3.651	1.427	2.560	3.758	1.479	2.541
14	0.3092	0.2497	0.4411	84.48	84.27	0.1366	0.1538	0.7096	0.1378	0.1535	0.7087	3.74	1.392	2.68	3.601	1.381	2.605	3.709	1.407	2.636
15	0.2659	0.3597	0.3744	85.00	84.91	0.1224	0.2309	0.6467	0.1278	0.2311	0.6411	3.75	1.395	2.69	3.563	1.337	2.665	3.697	1.370	2.699
16	0.4461	0.0887	0.4652	84.51	84.29	0.1896	0.0533	0.7571	0.1931	0.0566	0.7503	3.83	1.413	2.71	3.726	1.474	2.528	3.769	1.512	2.493
17	0.4402	0.1640	0.3958	85.38	84.94	0.2112	0.1103	0.6785	0.2054	0.1108	0.6838	3.57	1.401	2.55	3.703	1.448	2.557	3.745	1.473	2.542
18	0.3935	0.3081	0.2984	86.21	86.14	0.2095	0.2268	0.5637	0.2063	0.2244	0.5693	3.55	1.382	2.57	3.639	1.389	2.620	3.730	1.404	2.657
19	0.4955	0.3142	0.1903	87.68	87.80	0.3027	0.2710	0.4263	0.3019	0.2709	0.4272	3.66	1.411	2.60	3.685	1.415	2.604	3.751	1.411	2.658
20	0.5143	0.1144	0.3713	85.55	85.33	0.2498	0.0823	0.6679	0.2473	0.0818	0.6709	3.70	1.480	2.50	3.758	1.487	2.527	3.800	1.507	2.522
21	0.4697	0.4027	0.1276	88.68	89.09	0.3205	0.3776	0.3019	0.3150	0.3729	0.3121	3.46	1.373	2.52	3.647	1.381	2.642	3.697	1.367	2.704
22	0.5685	0.1624	0.2691	86.79	86.67	0.3110	0.1329	0.5561	0.3117	0.1323	0.5560	3.78	1.494	2.53	3.769	1.486	2.536	3.810	1.489	2.559
23	0.5816	0.2992	0.1192	89.08	89.19	0.4016	0.2948	0.3036	0.3990	0.2960	0.3050	3.69	1.427	2.59	3.730	1.442	2.586	3.733	1.421	2.627
24	0.6065	0.0041	0.3894	85.57	85.33	0.2879	0.0043	0.7078	0.2876	0.0030	0.7094	3.83			3.842	1.553	2.474	3.839	1.571	2.443
25	0.6152	0.1115	0.2733	86.80	86.75	0.3423	0.0929	0.5648	0.3370	0.0927	0.5703	3.71	1.496	2.48	3.810	1.518	2.510	3.834	1.518	2.526
26	0.0873	0.0808	0.8319	81.10	80.87	0.0289	0.0386	0.9325	0.0278	0.0350	0.9372	3.38	1.442	2.34	3.538	1.360	2.601	3.514	1.465	2.399
28	0.2309	0.0046	0.7645	81.69	81.48	0.0760	0.0019	0.9221	0.0761	0.0022	0.9217	3.66			3.659	1.451	2.521	3.614	1.523	2.373
29	0.0846	0.0723	0.8431	80.98	80.80	0.0261	0.0315	0.9424	0.0267	0.0311	0.9422	3.62	1.412	2.56	3.541	1.363	2.598	3.512	1.468	2.392
30	0.4391	0.0058	0.5551	83.59	83.57	0.1735	0.0042	0.8223	0.1749	0.0034	0.8217	3.75			3.716	1.472	2.525	3.768	1.553	2.426
31	0.2376	0.2095	0.5529	83.27	83.18	0.0984	0.1133	0.7883	0.0947	0.1146	0.7907	3.45	1.308	2.64	3.588	1.373	2.614	3.674	1.432	2.566
32	0.0077	0.1064	0.8859	80.52	80.42	0.0022	0.0395	0.9583	0.0024	0.0436	0.9540	3.66			3.456	1.315	2.628	3.467	1.442	2.404
33	0.0121	0.7902	0.1977	86.68	86.46	0.0076	0.5759	0.4165	0.0076	0.5746	0.4178	3.36	1.160	2.90	3.365	1.158	2.906	3.551	1.175	3.022
34	0.0104	0.6547	0.3349	84.93	84.88	0.0041	0.4022	0.5937	0.0054	0.4047	0.5899			2.89	3.393	1.190	2.850	3.585	1.224	2.929
36	0.0190	0.3234	0.6576	82.04	81.90	0.0064	0.1525	0.8411	0.0070	0.1525	0.8405			2.72	3.469	1.280	2.711	3.554	1.353	2.627
37	0.0183	0.2643	0.7174	81.85	82.26	0.0056	0.1269	0.8675	0.0065	0.1198	0.8737			2.52	3.429	1.276	2.687	3.595	1.374	2.616
42	0.7347	0.2475	0.0178	91.47	91.22	0.6370	0.3216	0.0414	0.6269	0.3151	0.0580		1.500		3.819	1.492	2.559	3.683	1.455	2.532
43	0.8249	0.1559	0.0192	91.79	91.76	0.7453	0.2048	0.0499	0.7231	0.2113	0.0656		1.454		3.898	1.546	2.521	3.703	1.503	2.462
44	0.7849	0.0616	0.1535	88.91	89.31	0.5362	0.0596	0.4042	0.5290	0.0657	0.4053	3.85	1.416	2.72	3.918	1.583	2.476	3.841	1.552	2.475
45	0.9035	0.0509	0.0456	91.43	91.60	0.7833	0.0657	0.1510	0.7740	0.0701	0.1559	3.82	1.487	2.57	3.991	1.608	2.482	3.765	1.553	2.424
46	0.6780	0.1711	0.1509	88.77	89.02	0.4526	0.1666	0.3808	0.4439	0.1787	0.3774	3.78	1.458	2.59	3.820	1.595	2.395	3.792	1.489	2.547
47	0.7883	0.1519	0.0598	90.73	90.77	0.6415	0.1813	0.1772	0.6282	0.1868	0.1850	3.64	1.468	2.48	3.882	1.543	2.516	8.752	1.499	2.503
48	0.7922	0.1942	0.0136	91.74	91.66	0.7154	0.2544	0.0302	0.6945	0.2594	0.0461		1.450		3.866	1.524	2.538	3.697	1.475	2.505
49	0.6695	0.3165	0.0140	91.32	91.27	0.5822	0.3872	0.0306	0.5663	0.3892	0.0445		1.407		3.758	1.454	2.585	3.673	1.413	2.599
50	0.6814	0.0773	0.2413	87.40	87.38	0.3983	0.0670	0.5347	0.3933	0.0691	0.5376	3.79	1.485	2.55	3.861	1.549	2.492	3.846	1.540	2.497
51	0.5988	0.3813	0.0199	90.90	90.81	0.5062	0.4381	0.0557	0.4938	0.4454	0.0608		1.360		3.705	1.417	2.616	3.673	1.381	2.660
52	0.2014	0.7834	0.0152	90.18	89.97	0.1721	0.7887	0.0392	0.1672	0.7909	0.0419		1.178		3.321	1.216	2.731	3.506	1.191	2.944
53	0.0621	0.9269	0.0110	89.87	90.27	0.0552	0.8979	0.0469	0.0533	0.9147	0.0320		1.088		3.390	1.150	2.948	3.466	1.130	3.068
54	0.1966	0.6573	0.1461	87.87	87.62	0.1300	0.5302	0.3398	0.1294	0.5367	0.3339	3.52	1.220	2.88	3.473	1.241	2.799	3.595	1.240	2.899
55	0.3852	0.5520	0.0628	89.62	89.77	0.2915	0.5354	0.1731	0.2884	0.5439	0.1677	3.64	1.283	2.84	3.567	1.316	2.710	3.618	1.296	2.792
56	0.0901	0.7733	0.1368	87.74	87.50	0.0621	0.6148	0.3231	0.0612	0.6224	0.3164	3.42	1.154	2.97	3.405	1.185	2.874	3.554	1.188	2.992
57	0.1634	0.4456	0.3910	84.81	84.57	0.0790	0.2678	0.6532	0.0777	0.2721	0.6502	3.46	1.246	2.78	3.497	1.284	2.723	3.635	1.321	2.752

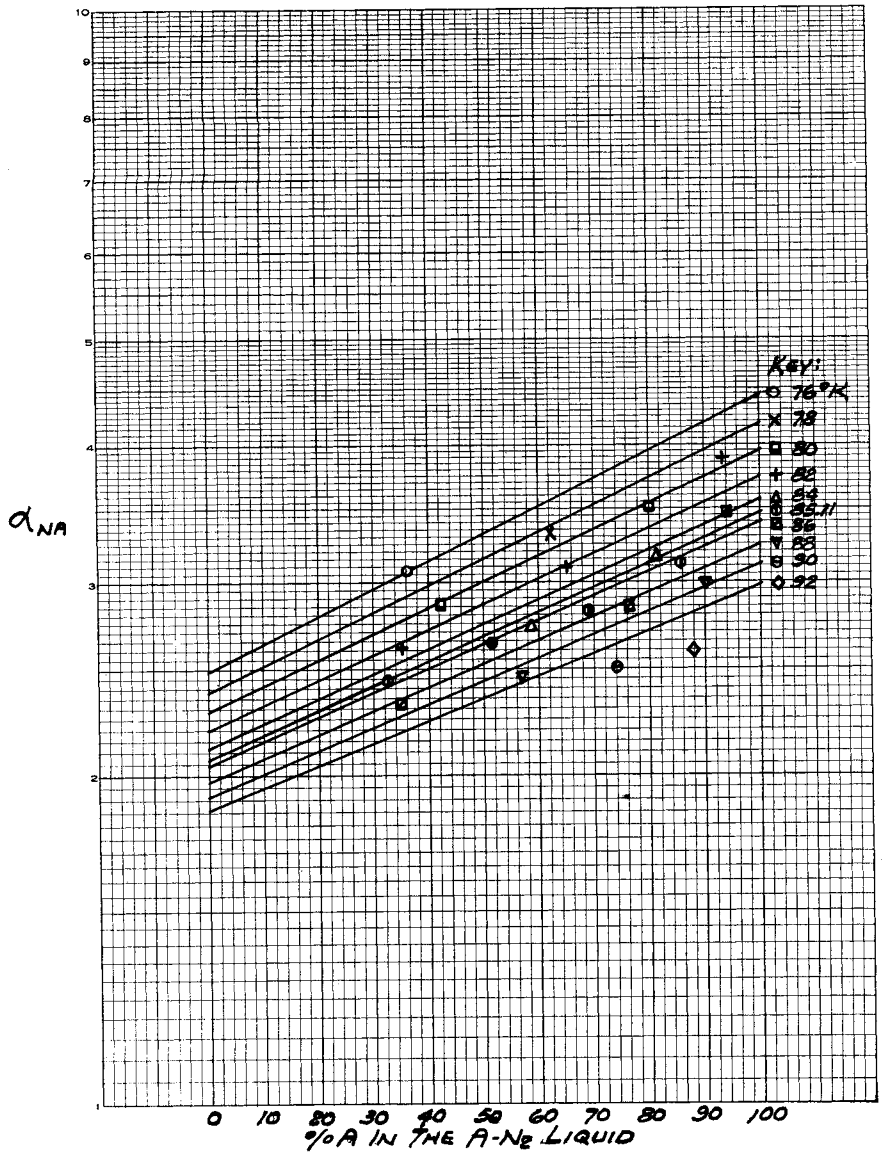

Fig. 5. Experimental α_{NA} binary data of Holst and Hamburger compared with author's correlation isotherms.

$$\log \alpha_{NO(50\text{-}50)} = \log \frac{f_{PN}^{0} e^{v_{LN}(\pi-P_N)/RT}/f_{\pi N}^{0}}{f_{PO}^{0} e^{v_{LO}(\pi-P_O)/RT}/f_{\pi O}^{0}} = -0.470 + \frac{88.4}{T} \tag{18}$$

$$\log \alpha_{AO(50\text{-}50)} = \log \frac{f_{PA}^{0} e^{v_{LA}(\pi-P_A)/RT}/f_{\pi A}^{0}}{f_{PO}^{0} e^{v_{LO}(\pi-P_O)/RT}/f_{\pi O}^{0}} = -0.132 + \frac{23.1}{T} \tag{19}$$

$$\log \alpha_{NA(50\text{-}50)} = \log \frac{f_{PN}^{0} e^{v_{LN}(\pi-P_N)/RT}/f_{\pi N}^{0}}{f_{PA}^{0} e^{v_{LA}(\pi-P_A)/RT}/f_{\pi A}^{0}} = -0.338 + \frac{65.3}{T} \tag{20}$$

$$\log \alpha_{NA(50\text{-}50)} = \log \alpha_{NO(50\text{-}50)} - \log \alpha_{AO(50\text{-}50)} = \log \frac{\alpha_{NO(50\text{-}50)}}{\alpha_{AO(50\text{-}50)}} \tag{21}$$

The fugacity ratios of Equations (18), (19), and (20) actually can be represented as a function of temperature by those equations over the entire binary-composition ranges, as these fugacity ratios are functions of temperature almost exclusively and are virtually unaffected by the limited pressure variation with composition at constant temperature. Therefore, by substituting these expressions for the fugacity ratios into Equation (12) and then combining Equation (15) with Equation (12), one obtains the following equations:

$$\log \alpha_{NO} = -0.470 + \frac{88.4 + c(x_O - x_N)}{T} \tag{22}$$

$$\log \alpha_{AO} = -0.132 + \frac{23.1 + c'(x_O - x_A)}{T} \tag{23}$$

$$\log \alpha_{NA} = -0.338 + \frac{65.3 + c''(x_A - x_N)}{T} \tag{24}$$

Thus for each binary combination, log α is linear with liquid composition for each isotherm. By plotting log α_{ik} against x_i for every experimental point along each isotherm for which experimental data are available, one can then select the value of constant c that results in a family of straight isotherms that reasonably well correlate the experimental data. This was done for Figures 5, 6, and 7, on which the families of straight lines are graphs of the following equations:

$$\log \alpha_{NO} = -0.470 + \frac{88.4 + 8.3(x_O - x_N)}{T} \tag{25}$$

$$\log \alpha_{AO} = -0.132 + \frac{23.1 + 7.5(x_O - x_A)}{T} \tag{26}$$

$$\log \alpha_{NA} = -0.338 + \frac{65.3 + 9.5(x_A - x_N)}{T} \tag{27}$$

These are the equations for relative volatilities of the respective binary mixtures. The 50-50 midpoint of each isotherm in Figures 5, 6, and 7 was established by Equations (18), (19), and (20) from vapor-pressure data and the generalized fugacity chart. Only the slope of each isotherm on Figures 5, 6, and 7 is dependent on the value assigned to the constant c in Equations 22, 23, and 24, which is determined from the experimental equilibrium data shown on those figures.

Figure 6 shows that a wealth of experimental equilibrium data are available for nitrogen-oxygen mixtures. The data at 65°, 70°, and 77.5°K. are by Armstrong, Goldstein, and Roberts (*1*). The data at 74.7° and 79.07°K. are by Inglis (*6*), and the data for 90.5°, 99.44°, 110.05°, 119.92°, and 125.0°K. are by Dodge and Dunbar (*3*). Figure 6 shows that Equation (25) represents all these data fairly well except those points approaching the 126.2°K. critical point of nitrogen (33.5 atm.).

Figure 7 shows the family of lines that was obtained by using a value of 7.5 for the constant c' in Equation (23) for argon-oxygen mixtures, resulting in Equa-

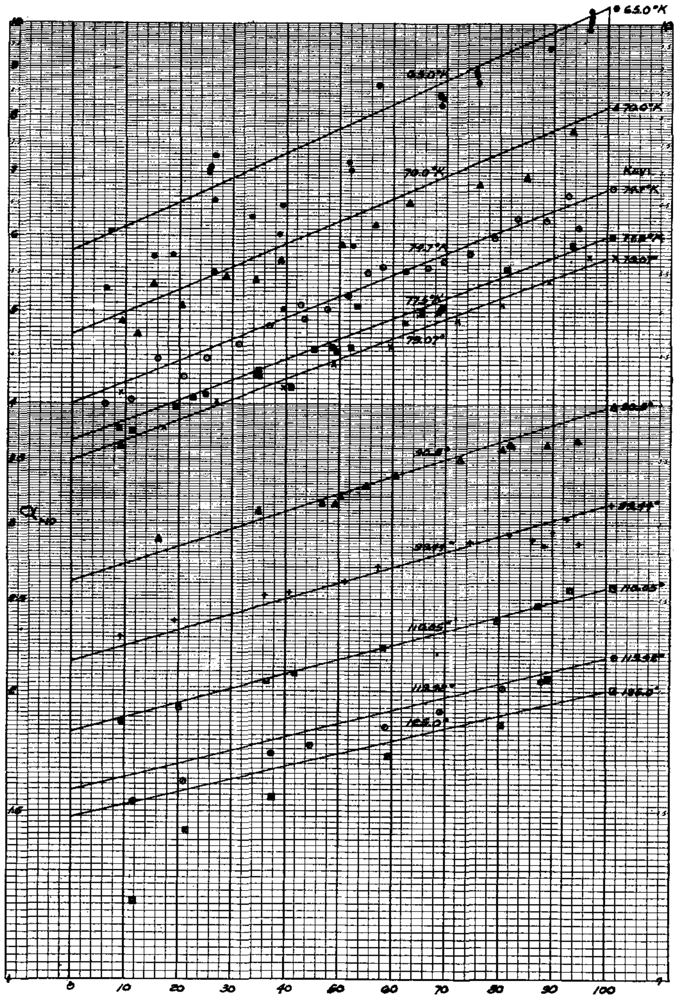

Fig. 6. Experimental α_{NO} binary data of Inglis, of Dodge and Dunbar, and of Armstrong et al. compared with author's correlation isotherms.

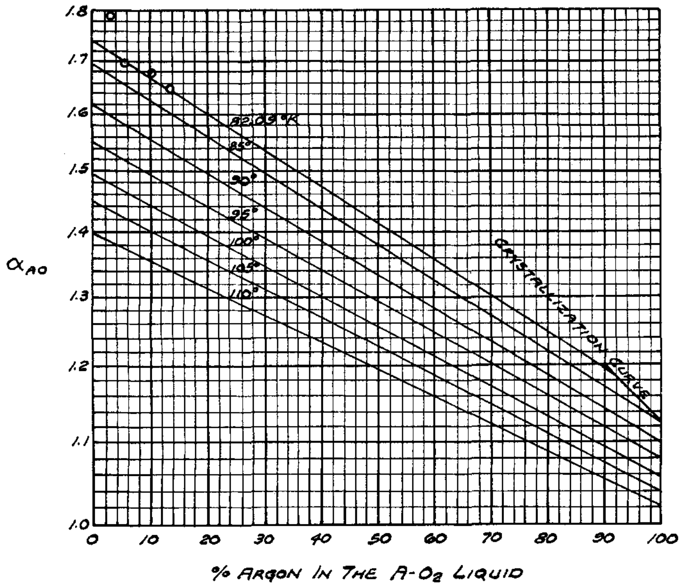

Fig. 7. Experimental α_{AO} binary data of Inglis compared with author's correlation isotherms.

tion (26). The straight lines for Figure 7 are plots of this equation. By selection of 7.5 for the numerical value of the constant, the 82.09°K. isotherm was made to pass through the fragmentary experimental data of Inglis (*6*) at 0 to 14% argon for that temperature. This value of the constant also resulted in location of the 90°K. isotherm so as to agree identically near 100% argon with carefully taken plant data. This value of the constant also resulted in location of the 95°K. isotherm on Figure 7 so as to agree reasonably satisfactorily with performance data from 0 to 15% argon in the liquid on ordinary and on very tall upper columns of air separating double columns, evaluated by the writer for cases for which the reflux ratio could be computed with considerable accuracy and for which a pinch condition was reached in this composition range. In this same composition and temperature range the Linde rectifying columns achieve separations which would be impossible, even with a very large number of trays, according to the experimental equilibrium data of Clark, Din, and Robb. The data of Clark, Din, and Robb therefore are not shown on Figure 7. The 100°, 105°, and 110°K. isotherms according to Equation (26) are plotted on Figure 7 for reference, although no Inglis or Linde data are available for checking them.

Equation (25) and the lines on Figure 6, which are plots of this equation, have been used for rectifying-column design since 1950 and Equation (26) and the lines plotted therefrom on Figure 7 have been used for design since 1954. They do not, however, differ greatly from the previous design data.

Figure 5 shows lines that resulted from selecting a value of $c'' = 9.5$ in Equation (24) for nitrogen-argon mixtures, resulting in Equation (27), so that the lines would agree on Figure 5 with Holst and Hamburger's (*4*) experimental data at 76° to 82°K. Unfortunately, data at temperatures increasing from 84° to 92°K. give relative volatility values differing increasingly downward from the lines for Equation (27). These look like systematic error in the Holst and Hamburger data, as Equation (20), on which Equation (27) is partly based, is believed to be accurately established by the Holst and Hamburger vapor-pressure data and by the Hougen and Watson (*5*) generalized fugacity chart. The midpoints of the isotherms shown on Figure 5 are established by the above-mentioned vapor-pressure data and fugacity chart, and the slopes of all the isotherms are established by choice of the constant 9.5 so as to agree with the low-pressure 76°-to-82°K. equilibrium data.

If Equations (25), (26), and (27) and the straightness of the isotherms on Figures 5, 6, and 7 are accepted as adequately established by the experi-

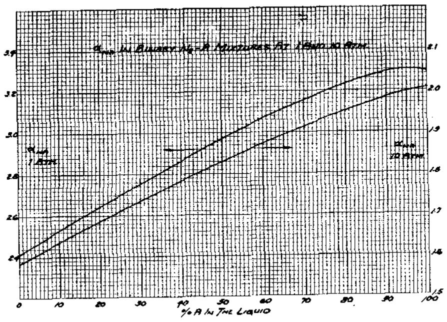

Fig. 8. α_{NA} in binary N_2 – A mxtures at 1 and 10 atm.

mental points on Figures 5, 6, and 7 and by the foregoing discussion, this acceptance verifies that the three binary systems nitrogen-oxygen, argon-oxygen, and nitrogen-argon form "regular" solutions and that in addition to Equations (25), (26), and (27) the following equations are also correct for these binary systems:

For nitrogen-oxygen mixtures:

$$T \log \frac{\gamma_N}{\gamma_O} = 8.3(x_O - x_N) \quad (28)$$

$$T \log \gamma_N = 8.3 x_O^2 \quad (29)$$

$$T \log \gamma_O = 8.3 x_N^2 \quad (30)$$

For argon-oxygen mixtures:

$$T \log \frac{\gamma_A}{\gamma_O} = 7.5(x_O - x_A) \quad (31)$$

$$T \log \gamma_A = 7.5 x_O^2 \quad (32)$$

$$T \log \gamma_O = 7.5 x_A^2 \quad (33)$$

For nitrogen-argon mixtures:

$$T \log \frac{\gamma_N}{\gamma_A} = 9.5(x_A - x_N) \quad (34)$$

$$T \log \gamma_N = 9.5 x_A^2 \quad (35)$$

$$T \log \gamma_A = 9.5 x_N^2 \quad (36)$$

In accordance with the equations in Wohl's (*10*) paper on liquid-phase activity coefficients for multicomponent mixtures, Equations (25) to (36) for the binary systems can be combined in a thermodynamically correct manner into the following equations for nitrogen-argon-oxygen ternary mixtures in general:

$$T \log \gamma_N = 9.5 x_A^2 + 8.3 x_O^2 + (9.5 + 8.3 - 7.5) x_A x_O \quad (37)$$

$$T \log \gamma_A = 7.5 x_O^2 + 9.5 x_N^2 + (7.5 + 9.5 - 8.3) x_O x_N \quad (38)$$

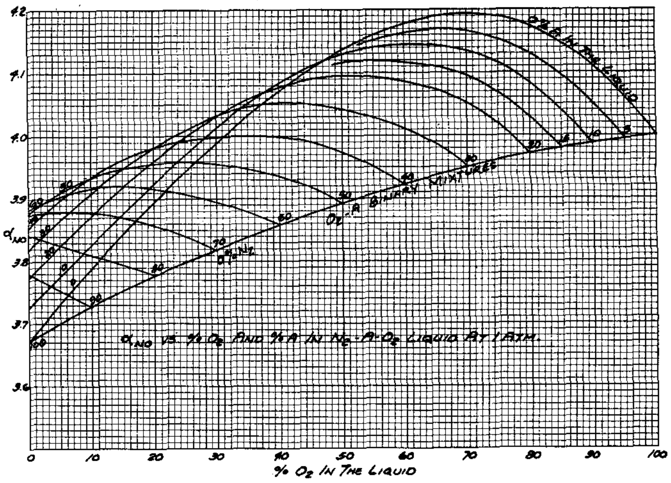

Fig. 9. α_{NO} vs. % O_2 and % A in N_2 – A – O_2 liquid at 1 atm.

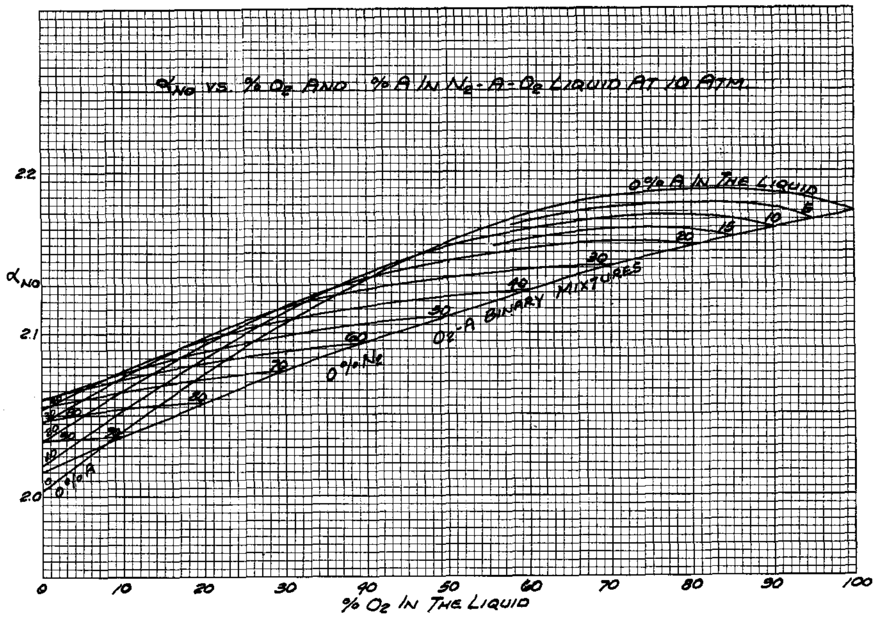

Fig. 10. α_{NO} vs. % O_2 and % A in N_2 – A – O_2 liquid at 10 atm.

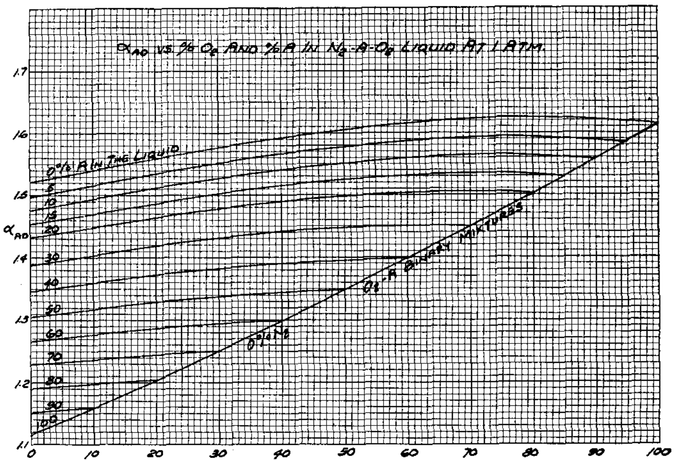

Fig. 11. α_{AO} vs. % O_2 and % A in N_2 – A – O_2 liquid at 1 atm.

$$T \log \gamma_O = 8.3x_N^2 + 7.5x_A^2 + (8.3 + 7.5 - 9.5)x_N x_A \quad (39)$$

$$T \log \frac{\gamma_N}{\gamma_O} = 8.3(x_O - x_N) + 2x_A \quad (40)$$

$$T \log \frac{\gamma_A}{\gamma_O} = 7.5(x_O - x_A) + 1.2x_N \quad (41)$$

$$T \log \frac{\gamma_N}{\gamma_A} = 9.5(x_A - x_N) + 0.8x_O \quad (42)$$

$$\log \alpha_{NO} = -0.470 + \frac{88.4 + 8.3(x_O - x_N) + 2x_A}{T} \quad (43)$$

$$\log \alpha_{AO} = -0.132 + \frac{23.1 + 7.5(x_O - x_A) + 1.2x_N}{T} \quad (44)$$

$$\log \alpha_{NA} = -0.338 + \frac{65.3 + 9.5(x_A - x_N) + 0.8x_O}{T} \quad (45)$$

Binary Equations (25) to (27) and ternary Equations (43) to (45) are consistent with the following identity:

$$\alpha_{NO}/\alpha_{AO} = \alpha_{NA} \quad (46)$$

The preceding equations are equations for "regular" solutions of nitrogen, argon, and oxygen.

VAPOR-LIQUID EQUILIBRIUM AS A FUNCTION OF PRESSURE AND COMPOSITION

The operation of a rectifying column is more nearly isobaric throughout than isothermal. Therefore, it is convenient for design purposes to combine the ternary vapor-pressure equations and graph of Figure 4 with the ternary equations for relative volatility as a function of temperature [Equations (43) to (45)], in order to get for design use equations and graphs of relative volatility as a function of pressure.

Equations (43) to (45) are of the form

$$\log \alpha_{ik} = f + \frac{g}{T} \quad (47)$$

for each liquid composition. The vapor-pressure equation is of the form

$$\log \pi = a - \frac{b}{T} \quad (48)$$

for each liquid composition. Combining Equations (47) and (48) gives

$$\log \alpha_{ik} = f + \frac{g}{\frac{b}{a - \log \pi}}$$

Rearranging gives

$$\log \alpha_{ik} = f + \frac{g}{b}(a - \log \pi) \quad (49)$$

Combining constants reduces this to

$$\log \alpha_{ik} = h - m \log \pi \quad (50)$$

Thus, the relative volatility is plotted vs. total pressure as a straight line on logarithmic graph paper for each liquid composition.

Therefore, from Figure 4 and Equations (43) to (45) the relative volatilities α_{NO} and α_{AO}, and α_{NA} for nitrogen-argon mixtures, were computed at 1 and 10 atm. and are plotted as a function of liquid composition on Figures 8 to 12 as the basis for construction of logarithmic graphs.

Figures 13 to 49* are logarithmic plots of α_{NO} and α_{AO}, and α_{NA} for the nitrogen-argon mixtures, against the total pressure in atmospheres absolute from 0.2 to 20 atm., with separate straight lines for each liquid composition. The entire ternary-composition range is covered, with separate lines for each 10% interval of percentage of argon and oxygen in the liquid. However, the α_{AO} graphs cover 5% intervals of percentage of argon, from 0 to 20% argon in the liquid. The points on each line for 1 and 10 atm. are plotted from Figures 8 to 12, and straight

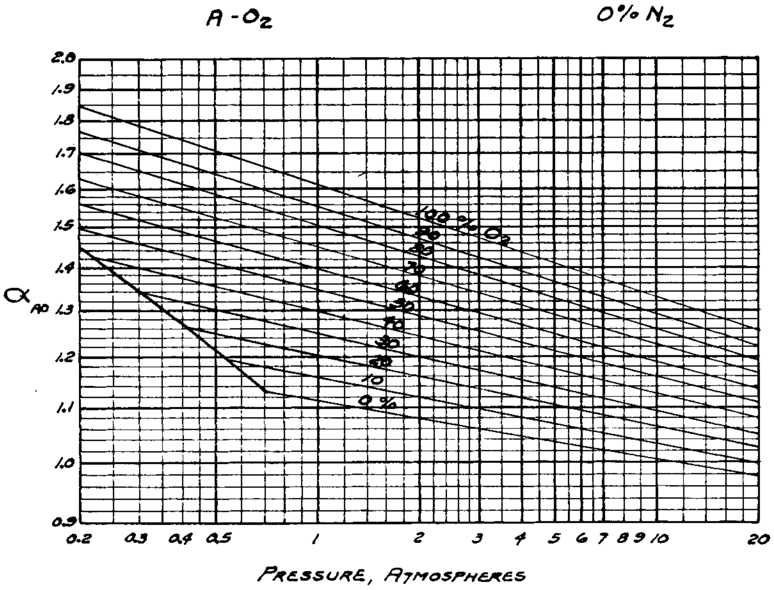

Fig. 33. α_{AO} vs. pressure and % O_2 in liquid for A-O_2 mixtures. (Figures 13 to 32 and 34 to 49 are plotted similarly to cover the entire N_2-A-O_2 composition range for α_{NO}, α_{AO}, and α_{NA} vs. pressure and liquid composition.

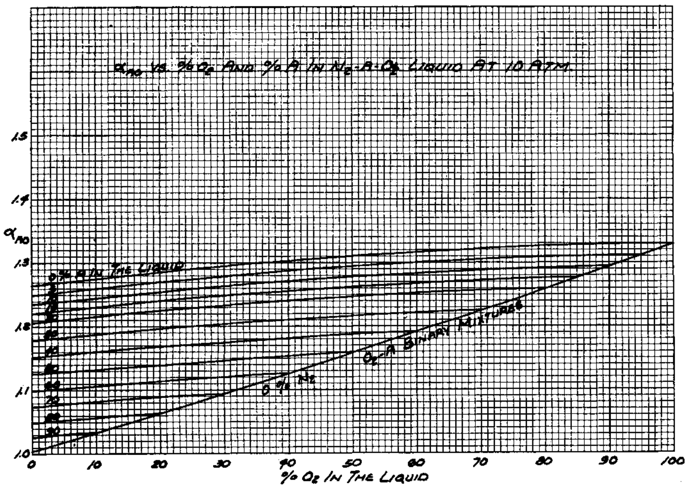

Fig. 12. α_{AO} vs. % O_2 and % A in N_2 – A – O_2 liquid at 10 atm.

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*See footnote on page 75.

Table 3

Mean Deviations of Weishaupt's Nitrogen-argon-oxygen Experimental Data from the Equations

	Deviation of experimental data from writer's equations					Deviation of experimental data from Weishaupt's equations			
	Δ_T	$\Delta\alpha_{NO}$	$\Delta\alpha_{AO}$	$\Delta\alpha_{NA}$	$\Delta\alpha_{all}$	$\Delta\alpha_{NO}$	$\Delta\alpha_{AO}$	$\Delta\alpha_{NA}$	$\Delta\alpha_{all}$
Absolute mean deviation	0.194°C.	0.122	0.047	0.109	0.091	0.106	0.060	0.114	0.092
Algebraic mean deviation	0.074°C.	−0.050	−0.024	−0.0006	0.025	−0.019	−0.012	0.004	0.012
Root mean square deviation		0.168	0.062	0.156	0.135	0.160	0.081	0.171	0.141

lines are drawn through these points from 20 down to 0.2 atm., or the crystallization curve.

The phase boundary between liquid and solid, that is, the crystallization point curve, is plotted on the diagrams from the experimental nitrogen-oxygen, argon-oxygen, and nitrogen-argon data of Ruhemann, Lichter, and Komarow (*8*) by use of straight-line interpolation of crystallization temperatures across the ternary diagram, as was done for the constants *a* and *b* in Figure 4.

Figures 13 to 49 are the working graphs of relative volatility for rectifying column design. However, it is convenient for the user to pick off values of relative volatilities at the pressure of his proposed rectifying column, and to plot them against percentage of oxygen, with separate curves for 0, 5, 10, etc., % argon, for the range of composition that he is concerned with. Then, in the tray-to-tray multicomponent rectification calculations [Lewis and Matheson (*7*)] values of the respective relative volatilities are read off the graphs and entered in the calculation for each tray for the liquid composition that exists at that point.

COMPARISON WITH WEISHAUPT'S NITROGEN-ARGON-OXYGEN EXPERIMENTAL DATA AND EQUATIONS

Weishaupt (*9*) measured the equilibrium vapor and liquid compositions for forty-three nitrogen-argon-oxygen mixtures at 1,000 mm. Hg and measured the saturation temperatures thereof. In Table 2 are tabulated the equilibrium liquid and vapor compositions and the measured temperatures compared with the temperatures computed by Figure 4. The measured relative volatilities α_{NO}, α_{AO}, and α_{NA} are compared for each point with the values from Equations (43) to (45).

Weishaupt presented approximate equations for the equilibrium vapor compositions at 1,000 mm. Hg only. It is of interest to compare at only this one pressure the experimental relative volatilities, the relative volatilities computed from Weishaupt's single-pressure equations, and the relative volatilities computed by the writer's general equations which cover the range from 0.2 to 20 atm. This is done in Table 2, and the results tend to confirm for ternary mixtures the reasonable degree of accuracy of the writer's equations.

The mean deviations of the experimental data from the writer's equations and from Weishaupt's equations are listed in Table 3, which shows that the writer's equations describe Weishaupt's experimental data approximately equally as well as Weishaupt's own equations do. The writer's equations have been shown to describe the vapor-liquid equilibrium not only at 1,000 mm. Hg, as Weishaupt's do, but over a wide range of pressure, insofar as binary equilibrium data are available with which to test them. The writer's equations, furthermore, have a sound thermodynamic basis, which is the safest way to describe such a system over a wide range of composition and pressure from a limited amount of available data.

ACKNOWLEDGMENT

A very large number of calculations were made by Phyllis M. Turner, who also plotted the computed points on the many diagrams. The drafting was done by Edna H. Saylor. The writer extends his appreciation to these coworkers and also wishes to thank Linde Air Products Company, in particular L. I. Dana and G. J. Boshkoff, for encouraging him to prepare this work for publication and for authorizing its publication.

NOTATION

e = base of the natural logarithms, 2.7182 - - -

f = fugacity of a component in a liquid or vapor solution

$f_P{}^0$ = fugacity of a pure component at its vapor pressure P

$f_\pi{}^0$ = fugacity of a pure component at the total pressure π of the mixture

p = partial pressure of a component in the vapor

P = vapor pressure of a pure component liquid or liquid mixture, atm. abs.

R = gas constant

T = absolute temperature, °K.

v_L = average molar volume of a pure liquid between its vapor pressure P and the total pressure π

x = mole fraction of a component in the liquid

y = mole fraction of a component in the vapor, especially the vapor in equilibrium with the liquid of composition x

α = relative volatility; defined by the following equation:

$$\alpha_{ik} = \frac{y_i/x_i}{y_k/x_k}$$

γ = activity coefficient of a component in the liquid phase

π = total pressure, atm. abs.

Subscripts

N = nitrogen

O = oxygen

A = argon

i and k = any components

Two subscripts for components used together, such as NO or *ik*, indicate that the property is for the first component listed relative to the second.

(50–50) = subscript indicating a liquid composition of 50% of each of the two components of a binary mixture

$a, a', a'', b, b', b'', c, c', c'', f, g, h,$ and m = arbitrary constants

Notation occurring only in Tables 2 and 3:

Subscripts r and x refer to the recommended equations of this paper and to Weishaupt's experimental data, respectively.

$\Delta\alpha$ = difference in relative volatility of one component with respect to another, according to two different sources of information.

The compositions shown in Table 1 and in all the graphs are liquid compositions.

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