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Chemical and Isotopic Equilibria Involving Liquid and Gaseous Nitrogen Oxides

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Existing experimental data dealing with liquid-gas-phase equilibria among the oxides of nitrogen (NO, NO_2, N_2O_3, and N_2O_4) have been re-examined, and an improved method has been developed for calculating the gas-phase composition for a given liquid phase and temperature. The method has been used to calculate chemical compositions in such systems over a wide range of temperature and total pressure. The effective single-stage separation factor for concentrating nitrogen-15 by this exchange system has also been evaluated over a broad range of operating conditions.

WHEN A LIQUID MIXTURE of oxides of nitrogen is equilibrated with its vapor, nitrogen-15 preferentially concentrates in the liquid phase. The effective single-stage fractionation factor, α_{eff}, of such an isotope exchange system depends on the temperature and pressure through two factors: The chemical compositions of the two phases depend upon the temperature and pressure; the quantum-mechanical distribution of isotopes among various chemical species is itself a function of temperature. The latter is directly calculable by the method of Bigeleisen and Mayer (*8*).

The exchange system, which consists of a liquid mixture of oxides of nitrogen and its vapor (hereafter referred to as the N_2O_3-NO system), was used by Monse *et al.* (*13, 15*) to prepare samples of highly enriched ^{15}N in an exchange column operated at atmospheric pressure. The effective single-stage separation factor ranged from 1.035 ±0.005 at −14° C. to 1.016 ± 0.004 at +14° C.

Monse *et al.* (*12*) further studied the effect of pressure on α_{eff} of the N_2O_3-NO system; it varied at 23° C. from 1.017 ± 0.002 at 2.1 atm. to 1.030 ± 0.002 at 7.4 atm. These authors (*13, 15*) also observed that nitrogen isotope exchange in this system is satisfactorily fast even at low temperature.

To facilitate examination of the most favorable conditions for concentrating ^{15}N using this system, we have carried out detailed digital computer calculations of chemical compositions and effective separation factor under widely varied equilibrium conditions.

CHEMICAL COMPOSITION

Beattie and coworkers (*2, 3, 5, 6, 7, 17*) have carried out extensive experimental and theoretical investigations of systems consisting of oxides of nitrogen (NO, NO_2, N_2O_3, and N_2O_4), with special emphasis on equilibria involving N_2O_3. Beattie and Vosper (*6*) measured the vapor pressure of liquid mixtures of nitrogen oxides of known compositions at various temperatures below 0° C., and were able to express their results in a form

$$\log_{10} p_{\text{mm}} = -\frac{f(x)}{T} + B(x) \qquad (1)$$

where p is the vapor pressure at T° K. of liquid containing an atom fraction x of +4 nitrogen. (In calculating x, N_2O_3 was regarded as consisting of an atom of +4 and an atom of +2 nitrogen.) No definite trend was found in $B(x)$; instead, its values seemed to be closely scattered around a value of 8.95. The coefficient of $1/T$, $f(x)$, was tabulated (*2, 6*) as a function of the liquid composition, ranging from $x = 1.00$ to $x = 0.525$. It was later extended down to $x = 0.505$ by Vosper (*17*). These results agree well with experimental results of Whittaker and coworkers (*18*), Purcell and Cheesman (*16*), and Baume and Robert (*1*). At $x = 1$, the results agree within 4% with vapor pressures of the N_2O_4-NO_2 system obtained by Giauque and Kemp (*9*).

The composition of the vapor in equilibrium with liquid mixtures of nitrogen oxides was studied by Beattie and Vosper (*7*) under various pressures and at a series of temperatures below −10° C. From their experimental results, the authors (*7*) concluded that the atom fraction of +4 nitrogen, y, in the vapor in equilibrium with liquid of a given composition appeared to be independent of temperature—that is, they were able to draw a single curve through plots of y *vs.* x, obtained at various temperatures. However, a re-examination of the results of Monse *et al.* (*12*) indicates that these authors' experimental results for x and y, obtained at room temperature, do not agree closely with Beattie and Vosper's curve. Since the present study was intended to cover a very wide range of temperature and pressure, requiring extensive extrapolation, we re-examined the apparent temperature-independency of the x-y relation by a series of equilibrium calculations.

Liquid-Vapor Equilibria. The composition of both phases was computed for every experimental point of Beattie and Vosper (*7*). For each experimental point, x, y, and the total pressure, p, were tabulated by those authors. [Tabulated values in (*7*) correspond to $(x + 1)$ and $(y + 1)$ in the present notation.] Using Beattie and Vosper's (*6*) vapor pressure relation,

$$\log_{10} p_{\text{mm}} = 8.95 - \frac{f(x)}{T} \qquad (2)$$

the corresponding equilibrium temperature was calculated.

In accordance with observations (*6, 7*) the liquid phase was assumed to consist only of N_2O_3 and N_2O_4. This sets a limitation on the applicability of the present model. First, the assumption immediately eliminates liquid-phase compositions smaller than $x = 0.5$; it is unable to handle liquids whose average composition corresponds to anywhere between pure NO and "pure" N_2O_3. Further, an analysis based on this assumption demands that y become zero as x approaches 0.5, instead of as x approaches zero. Fortunately, the region very close to $x = 0.5$ can be treated by a simpler analysis, so that this assumption is satisfactory for the present purpose. Then, the mole fractions of N_2O_3, x_3, and of N_2O_4, x_4, in a liquid of known x are given by

$$x_3 = 2(1 - x) \qquad (3)$$

and

$$x_4 = 2x - 1 \qquad (4)$$

Assuming ideality for the vapor phase, the following four relations exist among the partial pressures, p_1, p_2, p_3, and p_4, of NO, NO_2, N_2O_3, and N_2O_4, respectively.

$$P = p_1 + p_2 + p_3 + p_4 \qquad (5)$$

$$y = \frac{p_2 + p_3 + 2p_4}{p_1 + p_2 + 2p_3 + 2p_4} \qquad (6)$$

$$K_3 = \frac{p_1 p_2}{p_3} \qquad (7)$$

$$K_4 = \frac{p_2^2}{p_4} \qquad (8)$$

The total pressure, P, and the atom fraction of +4 nitrogen in the vapor phase, y, were provided by Beattie and Vosper's experimental observations (*7*). The equilibrium constant K_3 for the dissociation of N_2O_3,

$$N_2O_3 \rightleftharpoons NO + NO_2 \qquad (9)$$

was calculated from

$$\ln K_3^\circ \text{ (atm.)} = -\frac{4886.6}{T} + 17.116 \qquad (10)$$

and by assuming K_3 to be independent of pressure. Equation 10 was obtained from Beattie and Bell's (*3*) experimental data by a modified calculation (*4*). The equilibrium constant, K_4, for the dissociation of N_2O_4,

$$N_2O_4 \rightleftharpoons 2NO_2 \qquad (11)$$

was calculated by using the procedure recommended by Giauque and Kemp (*9*) with K_4° given by (*4*)

$$R \ln K_4^\circ \text{ (atm.)} = -\frac{12875.0}{T} + 2.9112 \ln T + 22.702 \qquad (12)$$

The Giauque and Kemp procedure calculates K_4 as $K_4 = 4(p_2 + p_4)\alpha'^2/(1 - \alpha'^2)$, where $\alpha' = \alpha + \beta(p_2 + p_4)$, in which $\beta = -0.01\ (294/T)^3$ and α is obtained from $K_4^\circ = 4(p_2 + p_4)\alpha^2/(1 - \alpha^2)$. Elimination of p_1, p_3, and p_4 from Equations 5 to 8 yields a cubic equation in p_2, which has only one positive root. The cubic equation was solved for p_2 by Newton's successive linear approximation procedure. Values of other unknowns were calculated accordingly. However, the procedure of Giauque and Kemp for obtaining K_4 made it necessary to iterate the entire process: In the first iteration, K_4° was used for K_4, and the resultant values of p_2 and p_4 were used to obtain a new value of K_4. The process was repeated until values of p_2 obtained by two successive iterations differed by less than 1×10^{-6} atm. From results of such calculations, ratios p_3/x_3 and p_4/x_4 were obtained at every point of Beattie and Vosper's tabulation. A plot of these ratios as a function of $1/T$ is shown in Figure 1. The solid lines represent a least-squares fit to the blackened points; the upper line is given by

$$\log_{10} \frac{p_4(\text{atm})}{x_4} = -\frac{1036.6}{T} + 0.95657 + 0.0082039\ T \qquad (13)$$

and the lower line is given by

$$\log_{10} \frac{p_3(\text{atm})}{x_3} = -\frac{1273.7}{T} + 1.96240 + 0.0065778\ T \qquad (14)$$

Points shown in Figure 1 by four rightmost open circles and four corresponding open triangles were rejected because they correspond to experimental points with x smaller than 0.520. The value 0.520 was chosen somewhat arbitrarily as a lower limit for the present model. Points represented by other open circles (and the corresponding open triangles) were omitted from the least-squares analysis because the circled points fall far from the least-squares line. Too much physical meaning should not be associated with the values of the least-squares constants in Equations 13 and 14. However, Figure 1 does show a high degree of correlation between the ratios and $1/T$. No obvious trends were found between the ratios and x at any given temperature.

Mole Fractions and Partial Pressures. The system under investigation has two degrees of freedom. With Equations 13 and 14 on hand, the most straightforward calculations of chemical compositions are achieved by specifying the temperature and x: The liquid phase mole fractions x_3 and x_4 are obtained from x using Equations 3 and 4. Equations 13 and 14 then lead to p_3 and p_4. The partial pressure of NO_2, p_2, is computed from p_4 by iteration, using Giauque and Kemp's procedure. The partial pressure of NO, p_1, is then calculated via Equation 7 with values of p_2 and p_3 obtained above. Having obtained all partial pressures, the total pressure, P, and the atom fraction of +4 nitrogen in the vapor phase, y, are calculated using Equations 5 and 6, respectively. As x approaches 0.5 in this model, y tends to zero, because p_1 thus calculated goes to infinity.

A representative excerpt of the results of these calculations is presented in Table I. In Figures 2 and 3, the total pressure calculated by the present method as a func-

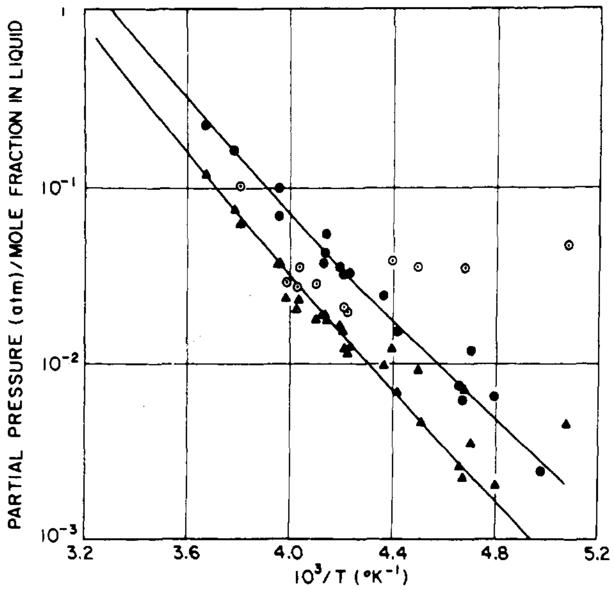

Figure 1. Ratio of partial pressure to mole fraction in liquid for N_2O_3 and N_2O_4 as a function of $1/T$

Points calculated for every experimental point of Beattie and Vosper (7)

● ○ N_2O_4

△ ▲ N_2O_3

○ and △ Omitted from least-squares-fit lines

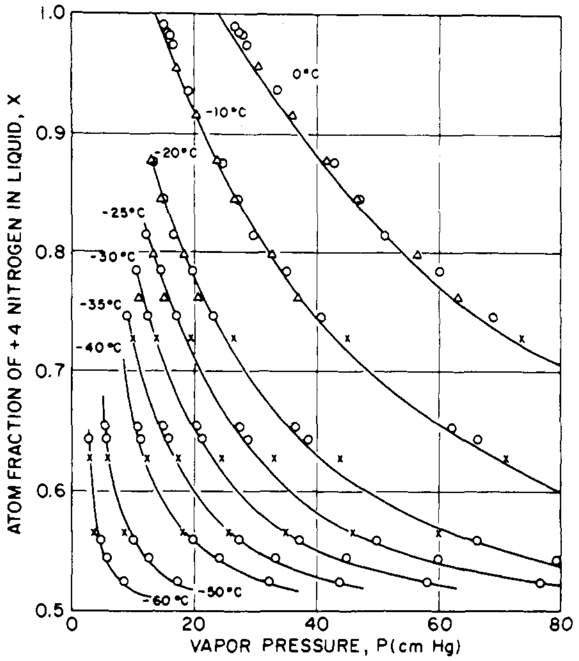

Figure 2. Vapor pressure of N_2O_3–NO system at various temperatures below 0° C.

○ Calculated from Eq. 1 (7)

△ Whittaker *et al.* (18)

× Purcell and Cheesman (16)

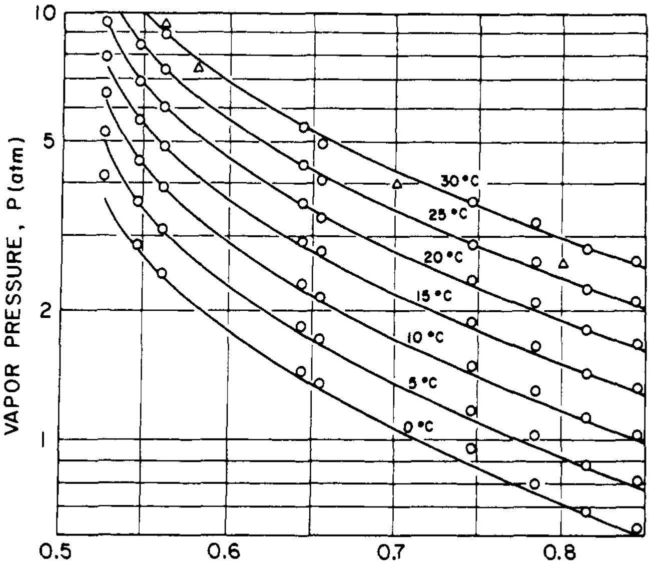

Figure 3. Vapor pressure of N_2O_3–NO system at various temperatures above 0° C.

○ Calculated from Eq. 1 (7)

△ Monse, Kauder, and Spindel (12)

Table I. Calculation of Vapor Phase Compositions of

Liquid			Temp., ° C.	Vapor						
x	x_3	x_4		p_1	p_2	p_3	p_4	y	P	α_{eff}
0.55	0.90	0.10	30	9.4517	0.1469	0.5121	0.1058	0.080	10.2164	1.0295
			20	6.2381	0.0793	0.3164	0.0669	0.075	6.7008	1.0315
			10	4.0141	0.0413	0.1910	0.0416	0.070	4.2880	1.0338
			0	2.5105	0.0207	0.1124	0.0253	0.065	2.6687	1.0362
			−10	1.5207	0.0099	0.0642	0.0150	0.062	1.6098	1.0388
			−20	0.8886	0.0045	0.0355	0.0087	0.058	0.9374	1.0416
			−30	0.4987	0.0019	0.0190	0.0049	0.056	0.5245	1.0446
			−40	0.2673	0.0008	0.0097	0.0027	0.054	0.2804	1.0480
			−50	0.1360	0.0003	0.0048	0.0014	0.053	0.1424	1.0516
			−60	0.0652	0.0001	0.0022	0.0007	0.052	0.0682	1.0556
			−70	0.0292	0.0000	0.0010	0.0003	0.052	0.0305	1.0599
0.60	0.80	0.20	30	5.9778	0.2064	0.4552	0.2115	0.144	6.8510	1.0293
			20	3.9389	0.1117	0.2813	0.1339	0.135	4.4657	1.0315
			10	2.5316	0.0582	0.1698	0.0831	0.127	2.8427	1.0338
			0	1.5819	0.0291	0.0999	0.0506	0.120	1.7614	1.0363
			−10	0.9576	0.0139	0.0571	0.0300	0.114	1.0587	1.0390
			−20	0.5593	0.0063	0.0316	0.0174	0.110	0.6146	1.0419
			−30	0.3138	0.0027	0.0169	0.0098	0.106	0.3431	1.0450
			−40	0.1681	0.0011	0.0086	0.0053	0.103	0.1832	1.0484
			−50	0.0855	0.0004	0.0042	0.0028	0.102	0.0930	1.0519
			−60	0.0410	0.0001	0.0020	0.0014	0.102	0.0445	1.0557
			−70	0.0184	0.0000	0.0009	0.0007	0.104	0.0199	1.0597
0.65	0.70	0.30	30	4.2998	0.2511	0.3983	0.3173	0.215	5.2665	1.0286
			20	2.8284	0.1361	0.2461	0.2008	0.203	3.4114	1.0309
			10	1.8156	0.0710	0.1486	0.1247	0.193	2.1599	1.0333
			0	1.1334	0.0356	0.0874	0.0758	0.184	1.3322	1.0358
			−10	0.6857	0.0170	0.0499	0.0450	0.176	0.7977	1.0385
			−20	0.4003	0.0078	0.0276	0.0261	0.170	0.4617	1.0414
			−30	0.2245	0.0033	0.0148	0.0146	0.165	0.2572	1.0444
			−40	0.1203	0.0013	0.0076	0.0080	0.163	0.1371	1.0476
			−50	0.0612	0.0005	0.0037	0.0042	0.162	0.0695	1.0510
			−60	0.0293	0.0002	0.0017	0.0021	0.163	0.0333	1.0545
			−70	0.0131	0.0001	0.0007	0.0010	0.168	0.0149	1.0580
0.70	0.60	0.40	30	3.2151	0.2878	0.3414	0.4231	0.293	4.2673	1.0274
			20	2.1112	0.1563	0.2109	0.2677	0.280	2.7462	1.0296
			10	1.3534	0.0817	0.1273	0.1663	0.268	1.7287	1.0320
			0	0.8441	0.0410	0.0749	0.1011	0.257	1.0610	1.0345
			−10	0.5102	0.0196	0.0428	0.0601	0.248	0.6327	1.0371
			−20	0.2977	0.0089	0.0237	0.0347	0.241	0.3651	1.0399
			−30	0.1669	0.0038	0.0126	0.0195	0.236	0.2029	1.0427
			−40	0.0894	0.0016	0.0065	0.0106	0.234	0.1080	1.0457
			−50	0.0454	0.0006	0.0032	0.0056	0.234	0.0547	1.0487
			−60	0.0218	0.0002	0.0015	0.0028	0.237	0.0262	1.0517
			−70	0.0097	0.0001	0.0006	0.0013	0.244	0.0118	1.0546
0.75	0.50	0.50	30	2.4150	0.3193	0.2845	0.5288	0.381	3.5476	1.0256
			20	1.5829	0.1737	0.1758	0.3347	0.367	2.2671	1.0277
			10	1.0133	0.0909	0.1061	0.2078	0.354	1.4182	1.0299
			0	0.6313	0.0456	0.0624	0.1264	0.342	0.8658	1.0322
			−10	0.3813	0.0219	0.0357	0.0751	0.332	0.5140	1.0347
			−20	0.2224	0.0100	0.0197	0.0434	0.325	0.2955	1.0372
			−30	0.1246	0.0043	0.0105	0.0244	0.320	0.1638	1.0398
			−40	0.0667	0.0017	0.0054	0.0133	0.318	0.0871	1.0424
			−50	0.0339	0.0007	0.0026	0.0069	0.320	0.0441	1.0450
			−60	0.0162	0.0002	0.0012	0.0035	0.325	0.0212	1.0474
			−70	0.0073	0.0001	0.0005	0.0017	0.335	0.0095	1.0495

[a] x and y represent atom fractions of +4 nitrogen in liquid and gas phases, respectively. P and p_i denote total and partial pressures,

tion of the liquid composition, x, at various temperatures is compared with experimental results of Beattie and Vosper (*6*), Whittaker *et al.* (*18*), Purcell and Cheesman (*16*), and Monse *et al.* (*12*). The points designated as Beattie and Vosper's were computed by using Equation 1. Figure 2 has been plotted using the same format as Beattie and Vosper (*6*) to permit a direct comparison of the two graphs. The agreement of the present calculation with the experimental values of the total pressure is remarkably good, especially in light of the fact that the present calculation is in a sense an open-ended one, in that P was obtained as the sum of the partial pressures of the various species. Particularly, at lower values of x, where nitric oxide is the major component in the gas phase, calculation of its partial pressure (obtained via Equation 7 from the ratio p_2/p_3) would be seriously affected by even a small mismatch of the two curves of Figure 1 (Equations 13 and 14). Since the calculations

N_2O_3–NO System for Various Liquid-Phase Compositions and Temperatures[a]

Liquid			Temp., °C.	Vapor						
x	x_3	x_4		p_1	p_2	p_3	p_4	y	P	α_{eff}
0.80	0.40	0.60	30	1.7781	0.3469	0.2276	0.6346	0.479	2.9873	1.0231
			20	1.1633	0.1891	0.1406	0.4016	0.465	1.8946	1.0249
			10	0.7436	0.0991	0.0849	0.2494	0.452	1.1770	1.0269
			0	0.4628	0.0498	0.0499	0.1517	0.440	0.7142	1.0290
			−10	0.2793	0.0239	0.0285	0.0901	0.430	0.4218	1.0311
			−20	0.1628	0.0109	0.0158	0.0521	0.423	0.2416	1.0333
			−30	0.0911	0.0047	0.0084	0.0293	0.419	0.1336	1.0355
			−40	0.0488	0.0019	0.0043	0.0159	0.417	0.0709	1.0377
			−50	0.0248	0.0007	0.0021	0.0083	0.420	0.0359	1.0397
			−60	0.0119	0.0002	0.0010	0.0042	0.427	0.0173	1.0414
			−70	0.0053	0.0001	0.0004	0.0020	0.439	0.0078	1.0428
0.85	0.30	0.70	30	1.2453	0.3715	0.1707	0.7404	0.588	2.5279	1.0199
			20	0.8131	0.2029	0.1055	0.4686	0.576	1.5900	1.0214
			10	0.5190	0.1065	0.0637	0.2910	0.563	0.9802	1.0230
			0	0.3226	0.0536	0.0375	0.1769	0.553	0.5906	1.0247
			−10	0.1945	0.0257	0.0214	0.1051	0.544	0.3468	1.0264
			−20	0.1133	0.0117	0.0118	0.0608	0.537	0.1977	1.0281
			−30	0.0634	0.0051	0.0063	0.0342	0.533	0.1090	1.0298
			−40	0.0339	0.0020	0.0032	0.0186	0.533	0.0578	1.0314
			−50	0.0172	0.0008	0.0016	0.0097	0.536	0.0293	1.0328
			−60	0.0083	0.0003	0.0007	0.0049	0.544	0.0141	1.0338
			−70	0.0037	0.0001	0.0003	0.0023	0.557	0.0064	1.0344
0.90	0.20	0.80	30	0.7836	0.3936	0.1138	0.8461	0.710	2.1372	1.0159
			20	0.5106	0.2154	0.0703	0.5355	0.700	1.3318	1.0169
			10	0.3254	0.1132	0.0424	0.3325	0.691	0.8136	1.0180
			0	0.2020	0.0570	0.0250	0.2022	0.682	0.4863	1.0192
			−10	0.1217	0.0274	0.0143	0.1201	0.675	0.2835	1.0203
			−20	0.0708	0.0125	0.0079	0.0695	0.669	0.1607	1.0214
			−30	0.0396	0.0054	0.0042	0.0390	0.667	0.0883	1.0225
			−40	0.0212	0.0022	0.0022	0.0212	0.667	0.0467	1.0234
			−50	0.0108	0.0008	0.0011	0.0111	0.671	0.0237	1.0241
			−60	0.0052	0.0003	0.0005	0.0056	0.678	0.0115	1.0246
			−70	0.0023	0.0001	0.0002	0.0027	0.690	0.0053	1.0246
0.95	0.10	0.90	30	0.3729	0.4136	0.0569	0.9519	0.847	1.7953	1.0111
			20	0.2425	0.2268	0.0352	0.6024	0.841	1.1069	1.0115
			10	0.1543	0.1194	0.0212	0.3741	0.835	0.6690	1.0119
			0	0.0957	0.0602	0.0125	0.2275	0.830	0.3959	1.0123
			−10	0.0576	0.0290	0.0071	0.1351	0.826	0.2288	1.0127
			−20	0.0335	0.0132	0.0039	0.0782	0.823	0.1289	1.0131
			−30	0.0187	0.0057	0.0021	0.0439	0.821	0.0705	1.0134
			−40	0.0100	0.0023	0.0011	0.0239	0.822	0.0373	1.0137
			−50	0.0051	0.0009	0.0005	0.0125	0.825	0.0190	1.0138
			−60	0.0024	0.0003	0.0002	0.0063	0.830	0.0092	1.0137
			−70	0.0011	0.0001	0.0001	0.0030	0.838	0.0043	1.0133
1.00	0.00	1.00	30	0.0000	0.4318	0.0000	1.0577	1.000	1.4894	1.0053
			20	0.0000	0.2373	0.0000	0.6694	1.000	0.9066	1.0049
			10	0.0000	0.1251	0.0000	0.4157	1.000	0.5408	1.0045
			0	0.0000	0.0632	0.0000	0.2528	1.000	0.3160	1.0040
			−10	0.0000	0.0304	0.0000	0.1501	1.000	0.1806	1.0035
			−20	0.0000	0.0139	0.0000	0.0869	1.000	0.1008	1.0030
			−30	0.0000	0.0060	0.0000	0.0488	1.000	0.0548	1.0025
			−40	0.0000	0.0024	0.0000	0.0265	1.000	0.0290	1.0020
			−50	0.0000	0.0009	0.0000	0.0139	1.000	0.0148	1.0016
			−60	0.0000	0.0003	0.0000	0.0070	1.000	0.0073	1.0012
			−70	0.0000	0.0001	0.0000	0.0033	1.000	0.0034	1.0008

respectively, in atm. Subscripts 1, 2, 3, and 4 refer to NO, NO_2, N_2O_3, and N_2O_4, respectively.

cover a very wide range of pressure and temperature, even a small change in slope, or displacement, of one of the curves in Figure 1, would lead to serious disagreement in some region of the range considered.

The total pressures thus obtained were fitted to the form

$$\log_{10} p_{mm} = -\frac{A(x)}{T} + B(x) + C(x)T \tag{15}$$

At least 10 points were used for the least-squares fit at any given x. These points were equally spaced in the temperature scale (rather than in the $1/T$ scale), ranging from the freezing point at the given x up to room temperature. Table II summarizes coefficients $A(x)$, $B(x)$, and $C(x)$.

In Figure 4, the calculated values of the gas-phase composition, y, are plotted against x at several, equally spaced, temperatures. The curves at −35° and −55° C.

Table II. Coefficients of Vapor Pressure Equation (Equation 15)

x	$A(x)$	$B(x)$	$C(x)$
1.000	973.72	3.0157	0.010724
0.950	1019.7	3.5907	0.0095936
0.900	1060.4	4.0880	0.0086458
0.850	1121.3	4.7022	0.0075219
0.800	1169.9	5.2150	0.0065986
0.750	1236.4	5.8489	0.0054759
0.700	1287.3	6.3691	0.0045776
0.650	1347.5	6.9658	0.0035628
0.600	1381.8	7.3913	0.0029101
0.575	1394.1	7.5836	0.0026560
0.550	1405.9	7.7962	0.0024097

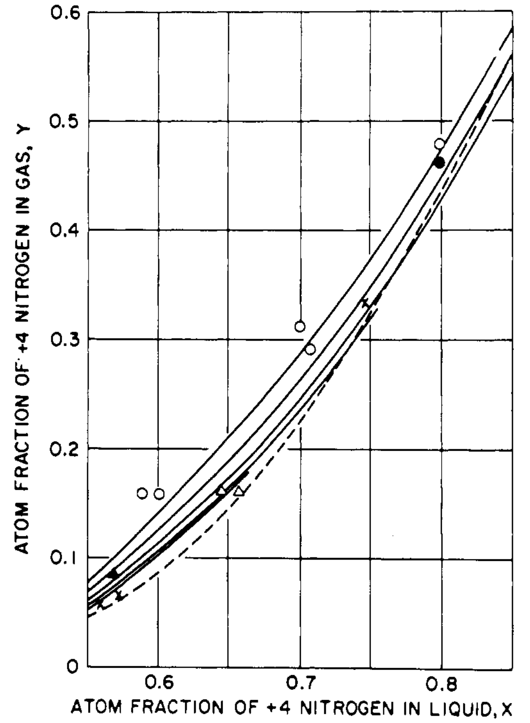

Figure 4. Vapor phase composition, y, as a function of liquid composition, x, at various temperatures

——— Present calculations at a series of temperatures: from top line to bottom, 25°, 5°, −15°, −35°, −55° C.
— — — Beattie and Vosper (7)
○ Monse, Kauder, and Spindel (12) at 24° ± 2°C.
● Purcell and Cheesman (16) at 5° C.
▲ Purcell and Cheesman at −15° C.
× Beattie and Vosper (6) at −35° ± 3° C.
△ Beattie and Vosper at −60° ± 2° C.

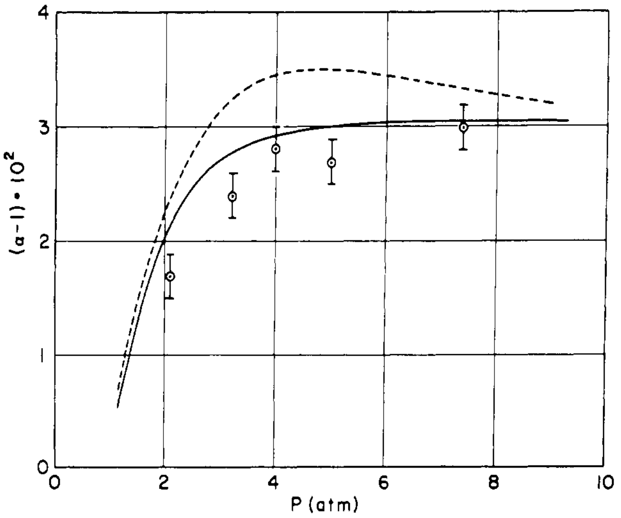

Figure 5. Effective isotope separation factor, α, as a function of total pressure at 23° C.

Experimental points from Monse, Kauder, and Spindel (12)
——— Present calculation
— — — Calculated by Monse, Kauder, and Spindel (11)

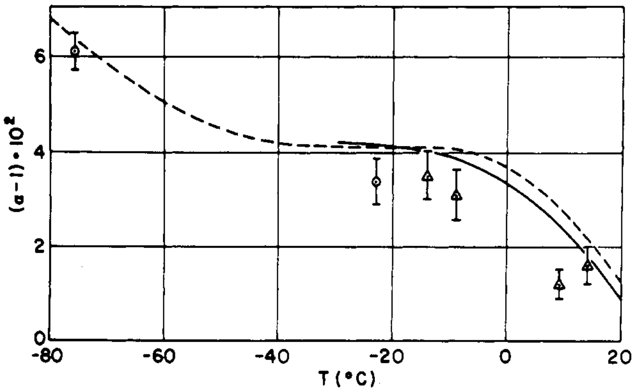

Figure 6. Effective isotope separation factor, α, as a function of temperature at 1-atm. pressure

○ Monse, Kauder, and Spindel (12)
△ Monse, Spindel, Kauder, and Taylor (13)
——— Present calculation
— — — Monse, Kauder, and Spindel (11)

terminate at the liquid compositions corresponding to those, whose freezing points are −35° and −55° C., respectively. While y is relatively insensitive to temperature changes, at any given liquid composition, in the lower temperature region studied by Beattie and Vosper (7) in establishing the x-y relation, the temperature dependence progressively increases with increasing temperature. Use of a temperature-independent x-y relation, therefore, will lead to increasingly erroneous results, especially at higher temperatures.

EFFECTIVE ISOTOPE SEPARATION FACTOR

The effective isotope fractionation factor, α_{eff}, for any gas-liquid exchange system, is given by

$$\alpha_{\text{eff}} = \frac{[\Sigma\, x_i(s/s'f)_i]_{\text{liq}}}{[\Sigma\, y_i(s/s'f)_i]_{\text{gas}}} \tag{16}$$

where the sum is over all chemical species present in each of the exchanging phases. Here x_i and y_i are the mole fractions of the ith chemical component in the liquid and gas phases, respectively. The $s/s'f$'s are the reduced partition function ratios for isotopically substituted molecules.

For nitrogen isotope exchange in the N_2O_3-NO system, Equation 16 contains two terms in the numerator for the liquid-phase species, N_2O_3 and N_2O_4, and four terms in the denominator for the gaseous species, NO, NO_2, N_2O_3, and N_2O_4.

The reduced partition function ratios, $s/s'f$, were calculated according to the Bigeleisen-Mayer formula,

$$\left[\frac{s}{s'}f\right] = \prod_i \frac{u_i}{u_i'}\,\frac{e^{-u_i/2}/(1 - e^{-u_i})}{e^{-u'_i/2}/(1 - e^{-u'_i})}$$

where $u_i = h\nu_i/kT$, in which ν_i is the ith frequency of a

Table III. Calculated Fundamental Vibrational Frequencies of Gaseous Oxides of Nitrogen[a]

^{14}NO	^{15}NO	$^{14}NO_2$	$^{15}NO_2$	$^{14}N_2O_3$	$^{15}N_2O_3$	$^{14}N_2O_4$	$^{15}N_2O_4$
1876.25	1842.70	1617.20	1581.35	1862.96	1828.97	1749.8	1711.3
		1318.44	1305.96	1588.67	1552.45	1715.5	1676.7
		750.34	739.80	1296.95	1288.01	1379.0	1355.5
				782.89	767.91	1261.4	1247.5
				627.03	610.66	804.4	795.4
				406.99	397.00	748.9	739.4
				312.92	310.33	660.6	641.8
				253.04	252.00	480.5	476.6
				35.00	34.62	441.6	431.3
						386.2	385.6
						267.3	265.8
						50.0	50.0

[a] All frequencies in cm^{-1}.
Frequencies of NO and NO_2 taken from Monse *et al.* (*14*); frequencies of N_2O_3 taken from Monse *et al.* (*11*); frequencies of N_2O_3 taken from Monse (*10*).

molecule. The product in the above equation is taken over all the normal vibrations, and u' and u refer to the lighter and heavier isotopic molecules, respectively. The ratio for a single isotopic substitution was obtained by first calculating $s/s'f$ for complete substitution of all nitrogen atoms in the given chemical species (double ^{15}N substitution for N_2O_3 and N_2O_4), and then raising the resulting values to the $1/n$th power (*11, 12*). Here n is the number of exchangeable nitrogen atoms per molecule. Effects of condensation on the partition function ratios of N_2O_3, and of N_2O_4 may be neglected (*11*). The fundamental frequencies of all the molecules used in the calculations are listed in Table III. These frequencies were taken from the literature cited in the table; all values were calculated by using a common force field for each chemical species.

The calculated values of the effective separation factor are tabulated in the last column of Table I. In Figure 5, the calculated values of α_{eff} (solid line) are compared with values experimentally obtained (*12*) at several total pressures, at 23° C. For comparison, values of α_{eff} calculated (*11*) by using the temperature-independent x-y relation are also shown as a dashed line in Figure 5.

The present calculations yield much better agreement with the experimental results. Figure 6 compares the calculated α_{eff} and the experimental results (*13, 15*) measured at various temperatures. Also shown in Figure 6 (dashed line) is α_{eff} calculated (*11*) by using the temperature-independent x-y relation. The curves level off in the mid-temperature range, below which the liquid phase becomes almost pure N_2O_3 and the gas-phase approaches pure NO; below this temperature the effect of change in composition becomes negligible, and the variation of α_{eff} with temperature is almost entirely due to the temperature-dependence of the partition function. The solid line in Figure 6 has been terminated at −30° C. because the liquid-phase composition becomes too close to that of N_2O_3 at lower temperature.

Results of calculations of the effective separation factor for other equilibrium conditions are summarized in Figures 7 and 8: In Figure 7, α_{eff} is plotted against x at various temperatures, and in Figure 8 it is plotted as a function of total pressure at various temperatures. For each temperature, in both figures, the liquid compositions covered, range from $x = 0.55$ to the freezing composition at that temperature. The crossovers of the plots of

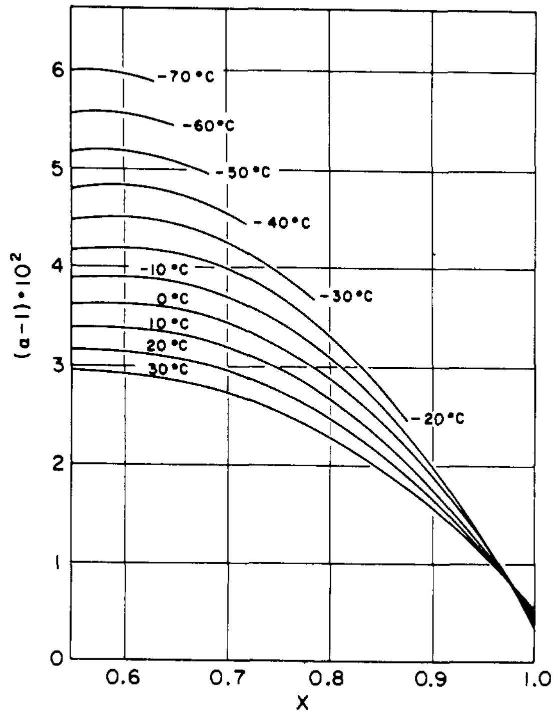

Figure 7. Effective isotope separation factor as a function of liquid composition, x, at various temperatures

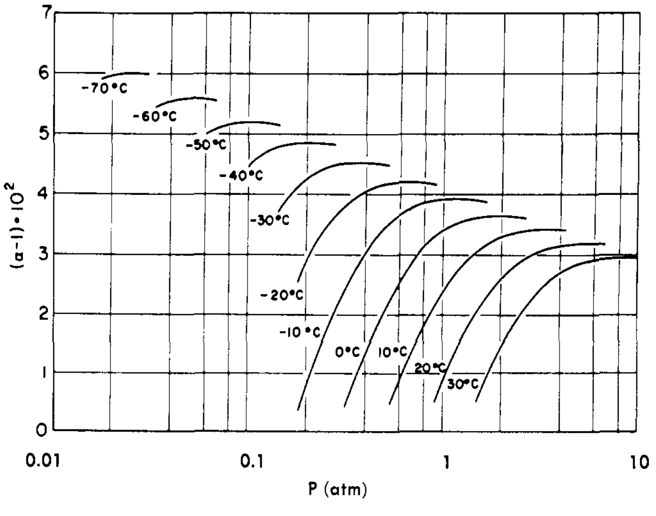

Figure 8. Effective isotope separation factors as a function of total pressure, at various temperatures

α *vs.* x (Figure 7) occurring at $x \sim 0.98$ are a direct consequence of the assumption that the liquid consists of N_2O_3 and N_2O_4 only. In this model, NO_2 is included in the gas phase, but its possible presence is ignored in the liquid phase.

The fact that a plot of α in Figures 7 and 8 goes over a maximum at any given temperature is not fictitious. The effective separation factor is increased by the addition of nitric oxide to the system, as long as the added NO affects the vapor phase—*i.e.*, decreases the denominator of Equation 16—more than the liquid phase. As the composition of the vapor phase approaches towards that of pure NO, a point is reached where further increase in the relative amount of +2 nitrogen in the system affects the gas phase composition less than the composition of the liquid phase; the numerator of Equation 16 decreases more rapidly than the denominator, and α_{eff} decreases.

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P-V-T Properties of Hydrogen and Mixtures Containing Hydrogen

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The generalized B-W-R equation of state of Edmister, Vairogs, and Klekers has been evaluated by them for a number of hydrocarbons with encouraging results. In the present work, the equation has been applied to hydrogen, which exhibits quantum deviations from the corresponding states principle, and to gas mixtures containing hydrogen. The systems examined in this paper are hydrogen, nitrogen-hydrogen, methane-hydrogen, and ethane-hydrogen.

THE BENEDICT-WEBB-RUBIN equation is an equation of state containing eight constants. These constants are derived empirically by fitting the equation to experimental *P-V-T* data. The equation is given below:

$$P = RTd + (B_0RT - A_0 - C_0/T^2)d^2 + (bRT - a)d^3 + a\alpha d^6 + (cd^3/T^2)(1 + \gamma d^2)\exp(-\gamma d^2) \quad (1)$$

where the constants of the B-W-R equation for hydrogen are (*8*):

$A_0 = 585.127$
$B_0 = 3.339\,37 \times 10^{-4}$
$C_0 = 482.82 \times 10^4$
$a = -98.597$
$b = 868.2 \times 10^{-4}$
$c = 1423.17 \times 10^3$
$a\alpha = 49.239$
$\gamma = 900.00 \times 10^{-3}$

These constants may be used in the B-W-R equation when T is in degrees Rankine, d in lb. moles per cu. ft., P in p.s.i., and $R = 10.7335$ lb. cu. ft. per (sq. in.) (lb. mole) (°R.).

W. C. Edmister and coworkers have generalized the above equation by expressing the eight constants as functions of critical temperature, critical pressure, and acentric factor (*5*):

$$^{m} = \theta\rho + (B_0'\theta - A_0' - C_0'/\theta^2)\rho^2 + (b'\theta - a')\rho^3 + a'\alpha'\rho^6 + (c'\rho^3/\theta^2)(1 + \gamma'\rho^2)\exp(-\gamma'\rho^2) \quad (2)$$

where[2] $\pi = P/P_c$
$\theta = T/T_c$
$\rho = dRT_c/P_c$

The constants of Equation 2 are functions of the acentric factor, ω. They are as follows:

$$A_0' = 0.343258 - 0.127521\omega - 0.509131\omega^2 \quad (3)$$

$$B_0' = 0.113747 + 0.127349\omega - 0.243280\omega^2 \quad (4)$$

$$C_0' = 0.098224 + 0.401236\omega - 0.0397267\omega^2 \quad (5)$$

$$a' = 0.0235866 + 0.290284\omega - 0.295413\omega^2 \quad (6)$$

$$b' = 0.0275404 + 0.131009\omega - 0.134924\omega^2 \quad (7)$$