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Arturo Maimoni and Donald N. Hanson

October 19, 1955

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ABSTRACT

This report presents data on index of refraction and liquid-vapor equilibrium for deuterium-nitrogen mixtures and compares them with the corresponding values for the hydrogen-nitrogen system.

The experimental techniques used to obtain the deuterium data are described in a previous Radiation Laboratory report[1] dealing with the measurements on hydrogen-nitrogen mixtures.

The index of refraction of deuterium for white light is slightly smaller than that of hydrogen: 1.80×10^{-6} index of refraction unit.

The index of refraction of deuterium-nitrogen mixtures is almost linear with composition and can be calculated within the limits of experimental error from the Lorentz-Lorentz molar refraction by using values of gas density corrected for the known deviations from ideal mixing behaviour.

Deuterium is slightly more soluble in liquid nitrogen than hydrogen; the relative volatility is 1.198 at 90°K and about 1.177 at 95°K.

The relative volatility is practically independent of pressure, thus, at 90°K, the relative volatility decreases from 1.198 at 100 psia to 1.196 at 1000 psia, but this range of values is well within the experimental error.

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INDEX OF REFRACTION

The data on index of refraction were obtained during the calibration of a Zeiss interferometer with 50-cm-long gas chambers, for use as an analytical tool for the subsequent liquid-vapor equilibrium measurements. The calibration was carried out by making synthetic blends of known composition, obtaining the corresponding interferometer reading, translating this reading into band numbers which are a direct measurement of the difference in index of refraction between the unknown and the reference gas, and correcting this value of band number to standard temperature and pressure.

The value of the corrected band number, designated as h_0, was found to be a linear function of composition and can be expressed by

$$x_c = 0.986567 - 0.0067845\ h_0 \qquad (1)$$

for deuterium-nitrogen mixtures read versus reference hydrogen, and

$$x_c = 0.0067705\ h_0 - 0.000135 \qquad (2)$$

for deuterium-nitrogen mixtures read versus reference nitrogen. Here x_c is the mol fraction of deuterium in the mixture calculated from the known value of h_0.

Values of x (the experimental composition), h_0, x_c (the calculated mol fraction), and the difference $x-x_c$ are tabulated in Tables I and II, and the values of $x-x_c$ are plotted for the different calibration blends in Figs. 1 and 2.

The composition of any unknown sample can thus be calculated from Eqs. (1) and (2) to within ±0.02 mole %. The internal consistency of the two sets of calibrations--i. e., those for hydrogen-nitrogen and those for deuterium-nitrogen--is very good, as evidenced by the following test: The equations for best fit to the two sets of data were calculated, and the

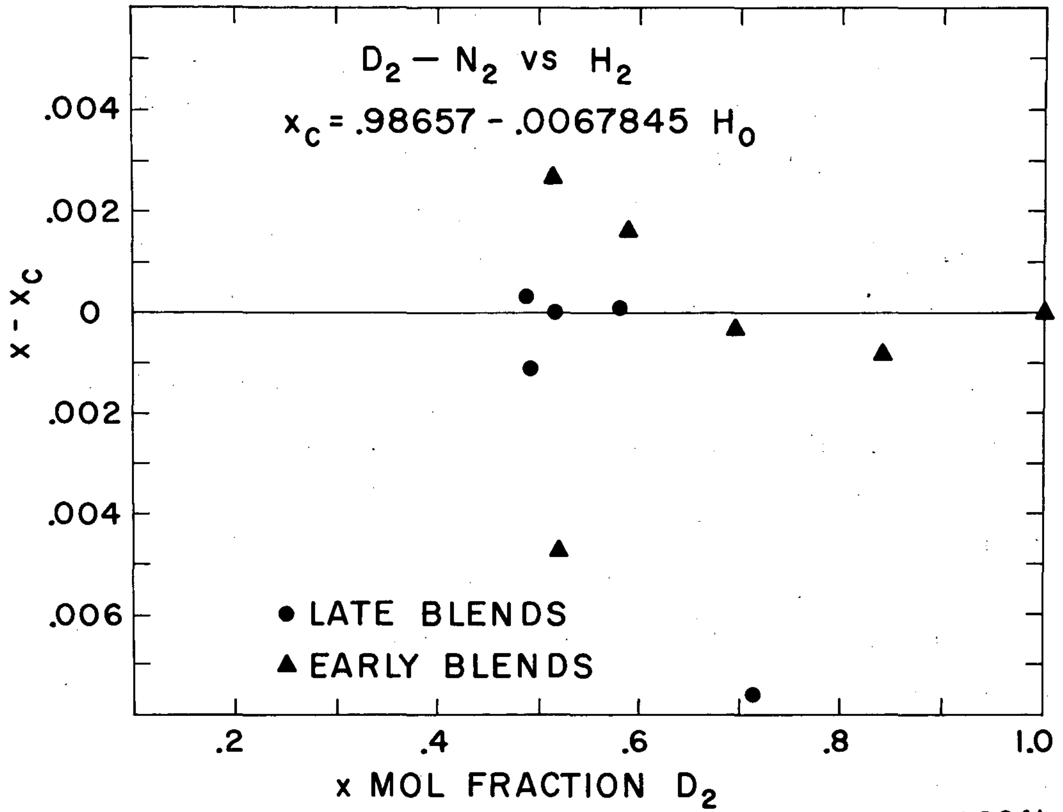

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Fig. 1. Index of refraction of deuterium-nitrogen mixtures read versus reference hydrogen.

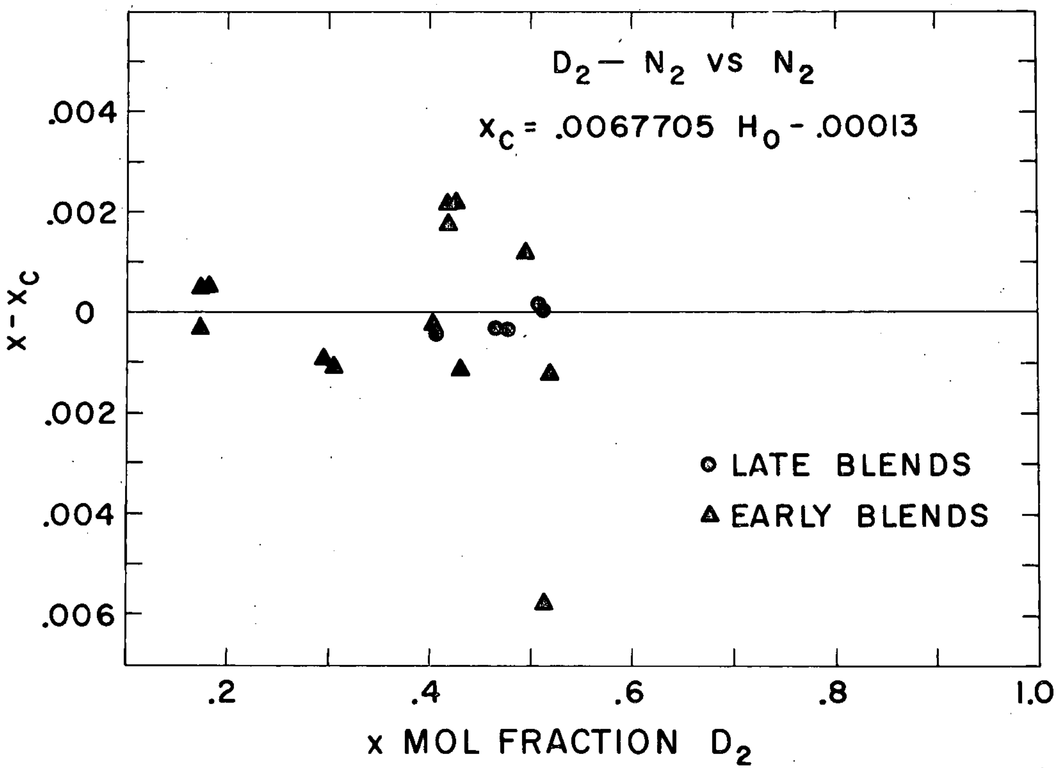

Fig. 2. Index of refraction of deuterium-nitrogen mixtures read against reference nitrogen.

coefficients of h_0 were compared after correcting the coefficient obtained from the hydrogen-nitrogen mixtures for the experimental value of the difference in index of refraction of deuterium and hydrogen. Thus, for blends read versus reference nitrogen;

coefficient of h_0 for best fit to D_2-N_2 blends = 0.0067700,
coefficient of h_0 from H_2-N_2 data, corrected = 0.0067709;

and for blends read versus reference hydrogen,

coefficient of h_0 for best fit to D_2-N_2 blends = 0.0067844,
coefficient of h_0 from H_2-N_2 data, corrected = 0.0067847.

It will be noted that the coefficient of h_0 for blends read versus reference nitrogen is somewhat different from the coefficient for blends read versus reference hydrogen. This small difference in the coefficients was explained for the H_2-N_2 system by the small deviations from the mixing behavior of ideal gases and was interpreted quantitatively, within the errors of the experimental data, by assuming linear molar refraction calculated from the correct value of molar volume of the mixture.

Since there is very good correspondence between the two sets of data, it may be concluded that the index of refraction of deuterium-nitrogen mixtures could also be calculated from the index of refraction of the pure components and the corrected value of the molar volume of the mixture.

LIQUID-VAPOR EQUILIBRIUM DATA

The liquid-vapor equilibrium data obtained for the deuterium-nitrogen system are tabulated in Table III and are compared with the corresponding hydrogen-nitrogen data in Figs. 3, 4, 5, and 6.

The liquid-vapor equilibrium constant K is plotted versus pressure for the two temperatures investigated, 90° and 95° K, in Fig. 3. Since this type of plot is not very convenient for accurate comparisons of the relative volatility of the hydrogen isotopes, some other method of plotting the data was devised. The function k', which is related to the Henry's law constant and is defined by

$$k' = \frac{x}{P - P^0_{N_2}}, \qquad (3)$$

where x is the mol fraction of neuterium in the liquid,

P is the total pressure, and
$P^0_{N_2}$ is the vapor pressure of pure nitrogen at

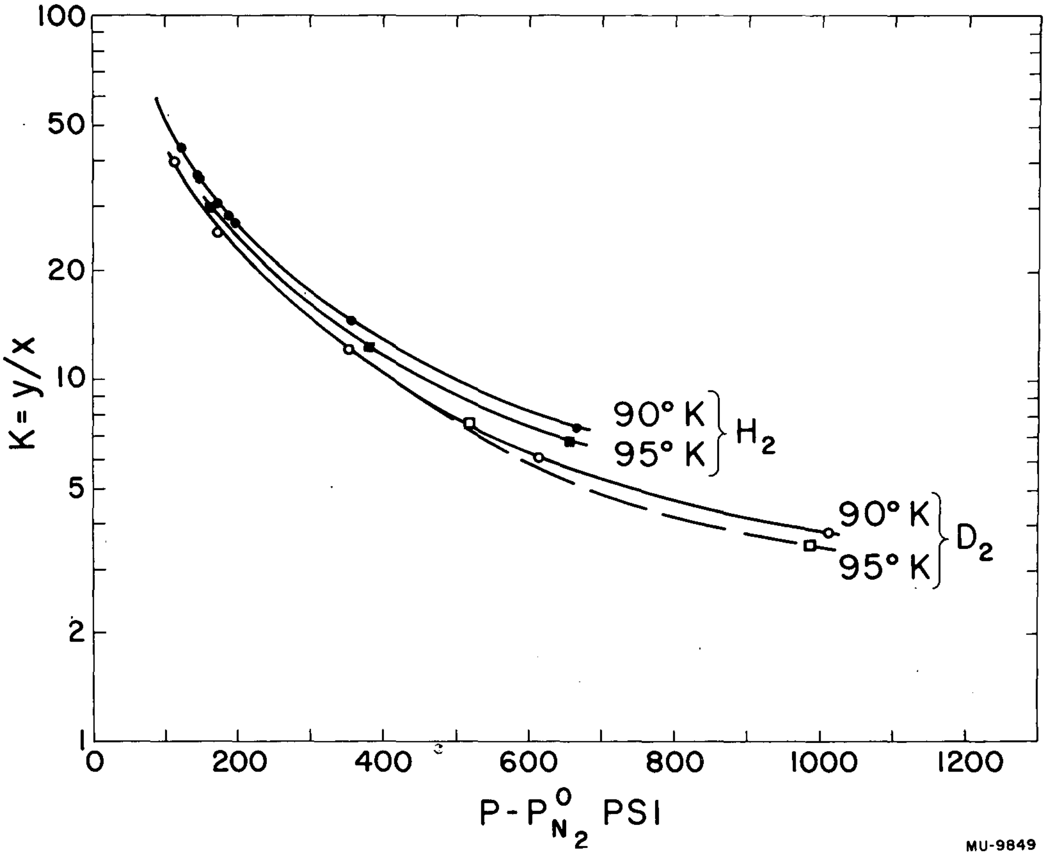

Fig. 3. Comparison of vapor-liquid equilibrium constants for hydrogen-nitrogen and deuterium-nitrogen systems.

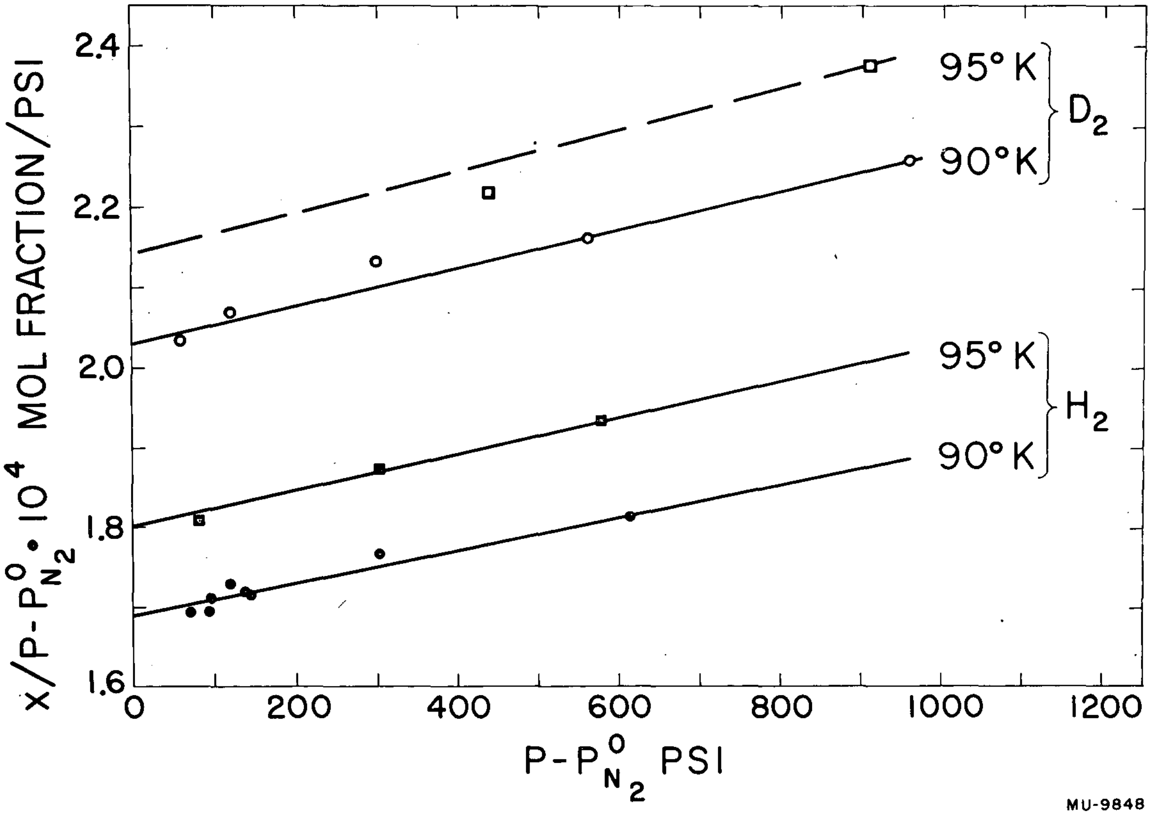

Fig. 4. Comparison of liquid compositions for deuterium-nitrogen and hydrogen-nitrogen systems.

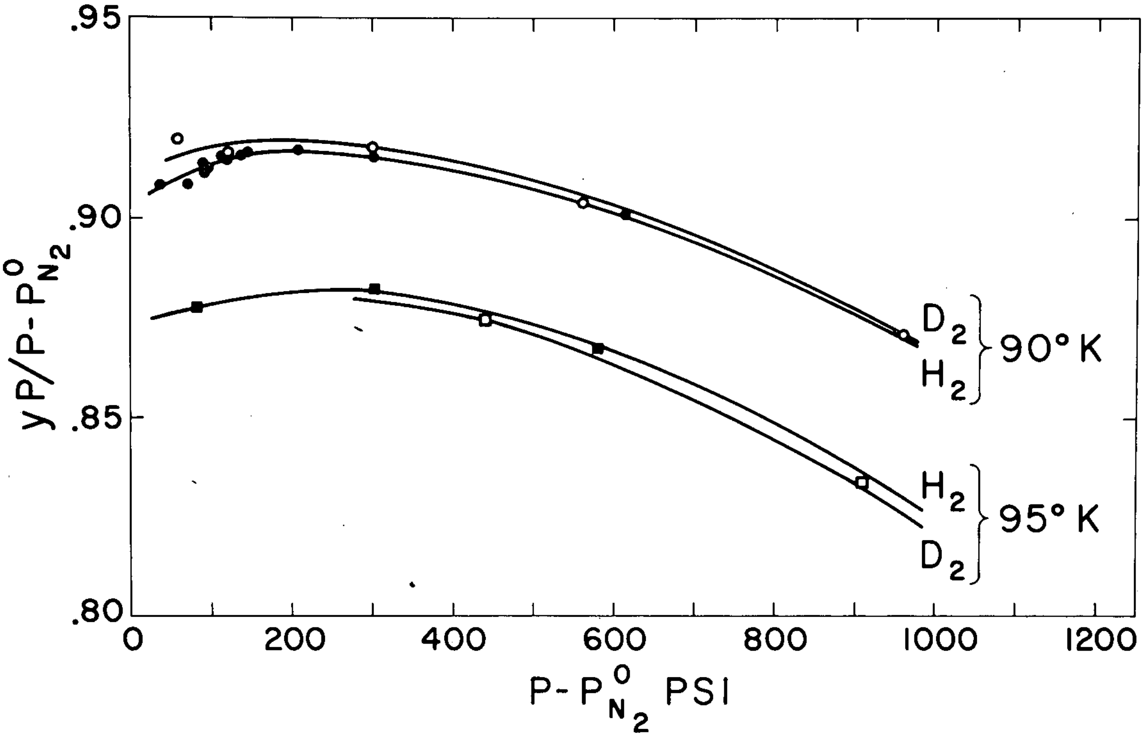

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Fig. 5. Comparison of vapor compositions for deuterium-nitrogen and hydrogen-nitrogen systems.

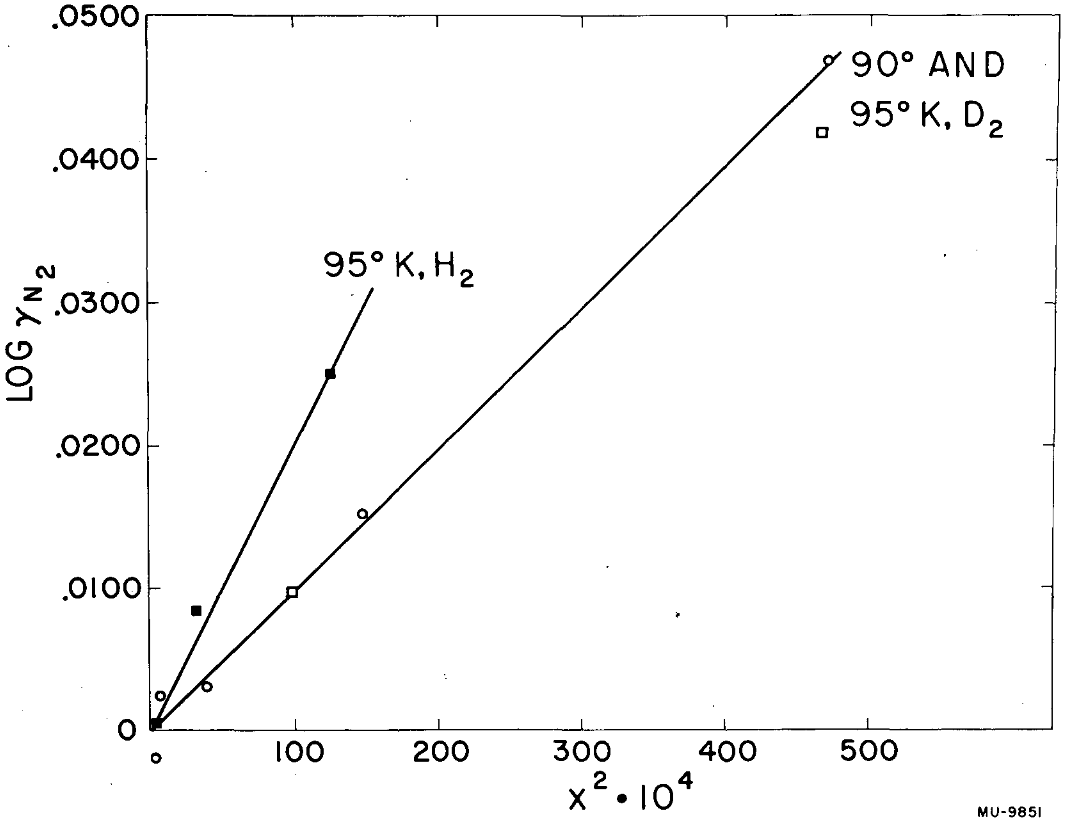

Fig. 6. Activity coefficient of nitrogen in the liquid phase.

the same temperature, is plotted in Fig. 4. This type of plot is very sensitive to liquid compositions and practically defines the value of the relative volatility, because there is very little difference in the composition of the vapors under the same conditions of temperature and pressure. The number of experimental points at 90° K is sufficient to determine accurately the value of k', but the time available for taking data was not sufficient for many experimental points at 95° K, where the value of k' for deuterium is less well defined.

The vapor compositions are plotted in Fig. 5, which shows the variation of the function

$$\frac{yP}{P-P^0_{N_2}}, \qquad (4)$$

where y is vapor composition in mol fraction. The function $yP/(P-P^0_{N_2})$ is convenient for smoothing isothermal data because it has a marked temperature dependence and varies slowly with pressure; it can be thought of as a measure of the deviations of the vapor phase from ideality. It may be seen that the vapor compositions are nearly identical.

Values of the relative volatility at a given T and P defined by

$$\alpha = \frac{x_D}{x_H} \cdot \frac{y_H}{y_D}, \qquad (5)$$

can be calculated from

$$\alpha = \left[\left(\frac{x}{P-P^0_{N_2}}\right)_{D_2} \Big/ \left(\frac{x}{P-P^0_{N_2}}\right)_{H_2}\right] \times \left[\left(\frac{yP}{P-P^0_{N_2}}\right)_{H_2} \Big/ \left(\frac{yP}{P-P^0_{N_2}}\right)_{D_2}\right].$$

The relative volatility at 90° K is practically constant across pressure at 1.198, decreasing to about 1.196 at 1000 psia total pressure, but this range of values is within the experimental error. At 95° K the relative volatility is not as well defined, owing to the scatter in liquid compositions; the value calculated from the point at 517.8 psia is 1.169 while the value at 987.7 psia is 1.185. The average of the two values is 1.177.

PURITY OF THE DEUTERIUM USED

The deuterium used was purified by circulating it over a bed of activated charcoal held at liquid nitrogen temperatures. A mass spectrographic analysis of the product follows:

$\frac{D}{H + D} = 99.63\%$

$\frac{H}{H + D} = 0.37\%$

H_2O, less than 0.1%, probably less than 0.01%

N_2 less than 0.1%, probably less than 0.01%

O_2 less than 0.04%, probably less than 0.01%.

TESTING OF THE DATA FOR THERMODYNAMIC CONSISTENCY

The experimental data were tested for thermodynamic consistency by using the same method as described for the hydrogen-nitrogen system, which involved the calculation of the activity coefficient of nitrogen in the liquid phase and examining its behavior across composition. The activity coefficient of nitrogen in the liquid phase was calculated from the liquid-vapor equilibrium data and the equations developed by Redlich[2], using the adjusted vapor pressure calculated from the equation of state by Redlich and Kwong[3].

For a nearly ideal solution, the activity coefficient can be expressed in terms of a single-constant equation of the form

$$\log \gamma_2 = B\ x_1^2, \qquad (7)$$

which indicates that a plot of log γ_2 vs x_1^2 should give a straight line going through the origin. It was considered that if this were the case with the data, the data could be considered thermodynamically consistent, since no other method could be developed to test the data for consistency. Figure 6 is a plot of log γ_{N_2} versus x^2, a plot that is indeed a straight line going through the origin, having a value of $B = 1.00$.

For the H_2-N_2 data, the line expressing the log γ_{N_2} at 90° K was slightly displaced from the 95° K line, which went through the origin; the displacement could be attributed to a systematic error in the vapor compositions of less than 0.2%. Since this effect is not present in the D_2-N_2 data, however, it may be concluded that the effect is probably due to deviations of the system from the properties predicted by the equation of state.

This work was done under the auspices of the U.S. Atomic Energy Commission.

Table I

Data for deuterium-nitrogen mixtures read versus reference hydrogen

Blend No.	x mol fraction	h_o band number	x_c* mol fraction	$x - x_c$ mol fraction
	1.0000	-1.98	1.0000	0
34	0.6938	43.10	0.6941	-.0003
44	0.5898	58.71	0.5882	+.0016
46	0.8397	21.52	0.8406	-.0009
49	0.5139	68.97	0.5186	-.0047
51	0.5048	71.40	0.5021	+.0027
68	0.4907	72.93	0.4918	-.0011
88	0.7048	40.41	0.7124	-.0076
89	0.4864	73.76	0.4861	+.0003
90	0.5139	69.67	0.5139	.0000
90	0.5780	60.23	0.5779	+.0001

* Calculated from $x_c = 0.9865667 - 0.0067845\, h_o$

Table II

Data for deuterium-nitrogen mixtures read versus reference nitrogen

Blend No.	x mol fraction	h_o band number	x_c^* mol fraction	$x - x_c$ mol fraction
37	0.4934	72.72	0.4922	+0.0012
38	0.2939	43.56	0.2948	-0.0009
42	0.1710	25.32	0.1713	-0.0003
43	0.3999	59.12	0.4001	-0.0002
48	0.1737	25.60	0.1732	+0.0005
52	0.1755	25.87	0.1750	+0.0005
53	0.3019	44.77	0.3030	-0.0011
56	0.5167	76.67	0.5189	-0.0022
57	0.4275	63.33	0.4286	-0.0011
58	0.4193	61.62	0.4171	+0.0022
59	0.4207	61.83	0.4185	+0.0022
60	0.5078	75.87	0.5135	-0.0057
62	0.4199	61.77	0.4181	+0.0018
63	0.5113	75.52	0.5112	+0.0001
64	0.5071	74.89	0.5069	+0.0002
65	0.4651	68.76	0.4654	-0.0003
66	0.4774	70.58	0.4777	-0.0003
67	0.4078	60.31	0.4082	-0.0004

* Calculated from $x_c = 0.0067705\ h_o - 0.000135$

Table III

Tabulation of liquid-vapor equilibrium data

D_2 - N_2

Run No.	T (oK)	P (psia)	$P-P_{N_2}^0$ (psi)	x (mol fraction)	y (mol fraction)	K = y/x	$\frac{x}{P-P_{N_2}^0}$ (x 10^4)	$\frac{yP}{P-P_{N_2}^0}$
	90.00	52.14*	0	0	0			
15-a	89.99	172.86	120.76	0.0250	0.6403	25.61	2.070	0.9165
15-b	90.05	112.29	59.94	0.0122	0.4910	40.24	2.035	0.9189
15-c	89.99	351.57	299.47	0.0639	0.7819	12.24	2.134	0.9179
15-d	90.05	613.40	561.03	0.1214	0.8268	6.810	2.164	0.9040
15-f	90.00	1011.59	959.45	0.2169	0.8264	3.810	2.261	0.8713
	95.00	78.13	0	0	0			
16-a	95.01	987.71	909.19	0.2160	0.7678	3.555	2.376	0.8341
16-b	95.00	517.83	439.40	0.9077	0.7446	7.621	2.223	0.8775

*Vapor pressure of nitrogen, by definition

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