Liquid-Vapor Equilibria in the Hydrogen-Nitrogen and Deuterium-Nitrogen Systems

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A recirculation type of apparatus with a novel liquid-sampling system was used to obtain liquid-vapor equilibrium data for the hydrogen-nitrogen and deuterium-nitrogen systems at 90° and 95°K. and pressures up to 1,000 lb./sq. in. abs. The data obtained show an average scatter in liquid compositions of the order of 0.01%, thus proving the feasibility of the new liquid-sampling system. The vapor samples are shown by thermodynamic analysis to scatter less than 0.1%. 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 lb./sq. in. abs. to 1.196 at 1,000 lb./sq. in. abs., but this range of values is well within the experimental error.

Vapor-liquid equilibrium data for the hydrogen-nitrogen and deuterium-nitrogen systems were needed to evaluated the feasibility of a process for separating the hydrogen isotopes by absorption in liquid nitrogen.

Since it was expected that the separation factor would be relatively low, it was considered essential to obtain accurate equilibrium data. For this reason a good deal of attention was given to the design of the experiment. After consideration of the different types of equipment which could have been used, it was decided to use the recirculation method, in which the vapor is repeatedly pumped through the liquid.

EQUIPMENT

Perhaps the only claim for novelty of the equipment used in this work is the liquid-sampling system. Most of the equipment described in the literature follows the design of Dodge and Dunbar (*2*), which avoids the complication of having a valve in the low-temperature section for sampling the liquid by having a long capillary line immersed in the liquid and having the liquid-sampling valve outside the cold thermostat. This procedure introduces uncertainty in the composition of the liquid sample owing to purging and the possibility of flashing of the liquid in the capillary line.

The liquid-sampling system used in this work is discussed with reference to Figure 1. The equipment is filled with gas by opening valve V-15 leading to the purification and storage manifold. Once the desired amount of gas is inside the equipment, the double-acting mercury-piston pump is turned on, forcing the gas to circulate along the path indicated by the heavier line in Figure 1. Meanwhile all the bypass valves, V-6, V-10, and V-11, are closed. After the gas leaves the pump, it passes through a rotameter to the cold thermostat, where the cooling coil cools it to the operating temperature of the thermostat. The gas then follows the path through V-7, PV-3, V-8, the liquid-sampling valve V-1, and V-9, and bubbles through the liquid in the equilibrium cell PV-1. After the vapor leaves the liquid, it goes through a series of baffles inside PV-1, which removes the liquid entrained. The gas leaving PV-1 goes through V-3 and then outside the cold thermostat to a heating coil in the intermediate water bath. From there it goes back into the main water bath and through V-4, V-2, PV-4, and V-5 back to the inlet of the pumps.

After sufficient time has been allowed for the vapor and liquid phases to come to equilibrium, the bypass valves, V-6, V-10, and V-11, are opened to flush the small amount of gas present in those lines with equilibrium gas. After about two min. of flushing the normal circulating path is resumed for another 5 min., and again the bypass valves are flushed. Then after sufficient time is allowed for the system to go back to equilibrium conditions, the liquid and vapor samples are taken as follows:

1. Valves V-11, V-10, and V-6 are opened consecutively.
2. Valves V-4 and V-5 are closed, which isolates the equilibrium vapor in PV-4. This vapor is sent later to the vacuum system for analysis by opening V-2 and V-16.
3. The liquid-level indicator (*10*) in PV-3 is turned on, then V-7 is closed, forcing the gas to circulate through V-10. The line coming from V-10 into PV-1 terminates well above the liquid surface, so that no active mixing of the liquid and vapor occurs during sampling. Then V-3 is partially closed, and the pressure drop through it forces the liquid at the bottom of PV-1 into the line leading to PV-3. When the liquid reaches PV-3, as indicated by the liquid-level indicator, valves V-8 and V-9 are closed, trapping about 2 ml. of liquid in the line. The liquid sample is sent to the vacuum system for analysis by opening V-1. The valves V-1, V-8, and V-9 were specially designed to minimize the possibility of trapping small bubbles of vapor in the line as the liquid flows up into PV-3.

While this liquid-sampling procedure is more complicated than the method used by Dodge, it removes all the uncertainties in the composition of the liquid sample mentioned before. It introduces uncertainties of its own however because of the possibility of having a vapor bubble trapped in the liquid-sampling line. This actually occurred before the correct adjusting procedure was found for the controls of the liquid-level indicator in PV-3. Fortunately the composition of the liquid samples thus obtained was in error by quite a few percent, so that these off samples were very easy to identify. Some of the other features of the equipment shown in Figure 1 are as follows.

The gas-sample reservoir PV-4 is a vessel of adjustable total volume, which allows for making small pressure adjustments in the system when running ternary or multicomponent mixtures. The volume adjustment is made with mercury which comes from a high pressure mercury reservoir located inside of the main water bath, and can be drained to the outside. Also since PV-4 is located very near the inlet of the reciprocating pump, its capacitance acts to damp the pulsations originating in the pump. The main water bath is used to keep a constant temperature in the gas reservoir and adjacent gas lines.

The intermediate water bath is used to warm to room temperature the gases coming from the cold thermostat; the high-pressure rotameter was used as a qualitative indication of flow through the equipment.

The equilibrium cell PV-1 is shown in more detail in Figure 2. The vapor coming from the bottom of the cell bubbles through the liquid and leaves through a fitting in the cap of the vessel. The temperature of the liquid is measured with a two-junction copper-constantan thermopile, which has at least 2 in. of bare wire in contact with the liquid to ensure a true reading of liquid temperature. The normal liquid level, as determined by the liquid-level indicator (*10*), is about 1 cm. above the inlet holes for the thermocouple wires, corresponding to an operating liquid volume of about 20 ml. The gas tube coming from V-10 ends just below the baffles.

Also shown in Figure 2 are the high pressure electrical connectors, which can be cooled repeatedly to liquid nitrogen temperatures without developing leaks.

Some of the remaining sections of the equipment require a more detailed description.

Cold Thermostat

The thermostat used in this work was designed for operation between 80°K. and room temperature. It was a recirculating gas thermostat cooled by direct injection of liquid nitrogen and controlled by a proportional plus reset type of controller

Table 1. Liquid-Vapor Equilibrium Data
H_2-N_2 system

Run no.	T, (°K.)	P, lb./sq. in. abs.	x (mole fractions) H_2	y
	90.00	52.14*	0	0
10	90.02	259.0	—	0.7324
11-a	90.02	196.76	0.0248	0.6732
11-b	90.01	188.20	0.0234	0.6619
11-c	90.03	171.91	0.0207	0.6367
11-d	90.02	164.42	—	0.6247
11-e	90.03	142.74	—	0.5791
11-f	90.04	148.07	0.0164	0.5903
11-g	89.99	122.35	0.0119	0.5217
11-h	90.01	88.96	—	0.3753
18-a	90.01	146.00	0.0159	0.5855
20-a	90.06	354.19	0.0534	0.7800
20-b	90.04	666.51	0.1115	0.8304
	95.00	78.43*	0	0
19-a	95.02	160.87	0.0149	0.4492
19-b	95.00	380.24	0.0566	0.7005
21-a	94.99	657.44	0.1121	0.7643

* Vapor pressure of nitrogen, by definition.

action, in which the proportional control was done with electric heaters while the reset action controlled the rate of liquid-nitrogen injection.

Temperature fluctuations in the equilibrium cell PV-1, due to erratic control action, were of the order of 0.005°C. during a run.

Temperature Measurement

Temperatures at various locations were measured with copper-constantan thermocouples and read with a potentiometer.

While the thermocouples used were not calibrated in terms of the vapor pressure of oxygen and the international temperature scale, the temperatures as used in this work are defined in terms of the vapor pressure of pure nitrogen and the table of vapor pressure of nitrogen, (*11*) as follows:

Temperature (°K.)	Vapor pressure (lb./sq. in. abs.)
90.000	52.140
95.000	78.430

Pressure Measurement

The operating pressure for each run was determined to the nearest 0.02 lb./sq. in. abs. with a dead-weight gauge. The ultimate limit of sensitivity of the gauge was about 0.002 lb./sq. in. abs. The reproducibility of the gauge, as shown by repeated calibrations, was better than 0.02 lb./sq. in. abs. and the maximum measurable pressure about 2,200 lb./sq. in. abs.

The gauge was calibrated at low pressures against a mercury manometer and at the carbon dioxide point (507.577 lb./sq. in. abs.). The carbon dioxide used in the calibration was specially purified, analyzing better than 99.993% by mass spectrographic analysis.

Equipment for Purification and Storage of Gases

The section used for purification and storage of the gases used was built in as a permanent part of the equipment. The purification of the gases, in this case hydrogen and nitrogen, was accomplished by passing the raw gas at high pressure and a slow rate through a bed of activated charcoal held at a temperature low enough to remove most of the higher-boiling impurities of the raw gas; thus for nitrogen purification the bed was held at dry-ice temperature, while for hydrogen purification the bed was cooled with liquid nitrogen. The purification vessel was heated to 100°C. to help in outgassing the charcoal, while the entire manifold and purification systems were evacuated before starting the purification procedure.

This method of purification seemed to be quite effective, as evidenced by the following mass spectrographic analysis of a typical sample of purified gases. It should be noted that the amounts of impurities recorded below are the maximum limits of impurities in the sample, with the assumption that the mass spectrograph has zero background.

Gas	D_2	H_2	N_2
A			0.022
O_2	0.01	0.004	0.004
N_2	0.01	0.009	99.974
H_2	0.37	99.970	
D_2	99.61	0.002	
HD		0.015	
	100.00	100.000	100.000

Gas Analysis

The analysis of the gas and liquid samples was made with an optical interferometer with 50 cm. long gas chambers (*5*) which was calibrated with mixtures of known composition prepared in a specially designed gas blending apparatus (*6*).

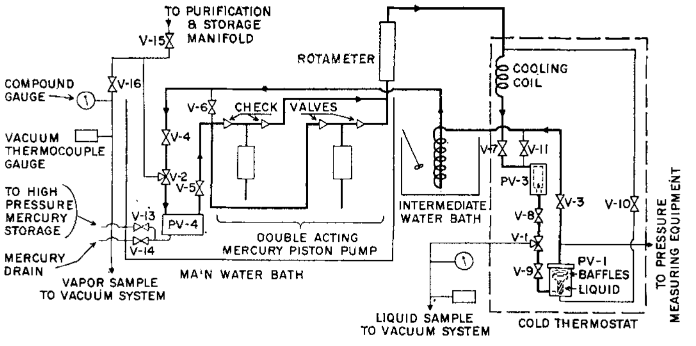

Fig. 1. Flow diagram of recirculation equipment.

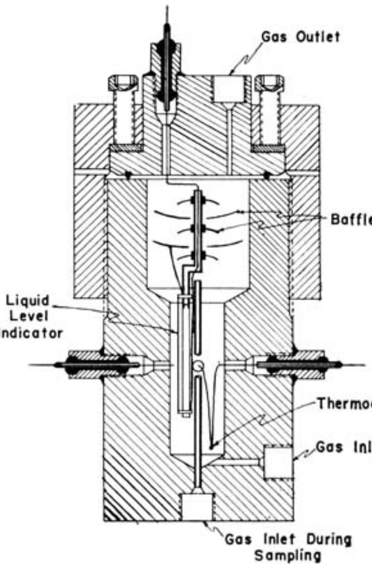

Fig. 2. Equilibrium cell, PV-1.

TIME FOR APPROACH TO EQUILIBRIUM

The time required for a given approach to equilibrium in a recirculation type of apparatus is short and can be calculated if one assumes that all the vapor is concentrated in a reservoir and that there is perfect mixing of the gas in the reservoir.

The calculation shows that the time required to approach the equilibrium composition within 0.01% is at the most 15 min., which is a relatively short time for equilibrium measurements of this nature.

In practice about 1 hr. was allowed for thermal equilibrium of the system, and samples were withdrawn after the pressure remained steady (± 0.01 lb./sq. in.) for 10 min.

EXPERIMENTAL RESULTS

The time available for taking data was limited; therefore the following results include only the 90° and 95°K. isotherms up to a pressure of about 1,000 lb./sq. in. abs. The results are listed Tables 1 and 2.

Table 2. Liquid-Vapor Equilibrium Data
D_2-N_2 system

Run no.	T, (°K.)	P, lb./sq. in. abs.	x (mole fractions)	y
	90.00	52.14*	0	0
15-a	89.99	172.86	0.0250	0.6403
15-b	90.05	112.29	0.0122	0.4910
15-c	89.99	351.57	0.0639	0.7819
15-d	90.05	613.40	0.1214	0.8268
15-f	90.00	1011.59	0.2169	0.8264
		78.43*	0	0
16-a	95.01	987.71	0.2160	0.7678
16-b	95.00	517.83	0.9077	0.7446

* Vapor pressure of nitrogen, by definition.

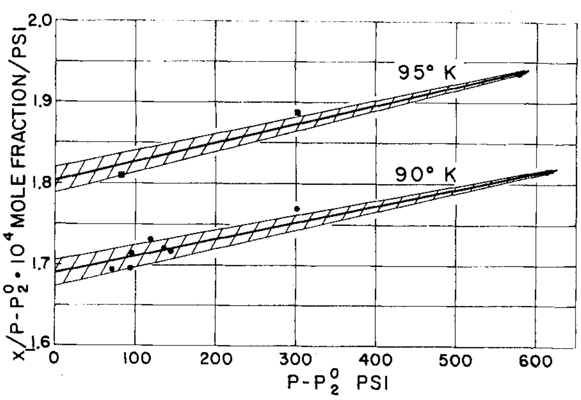

Fig. 3. Hydrogen-nitrogen system: liquid compositions.

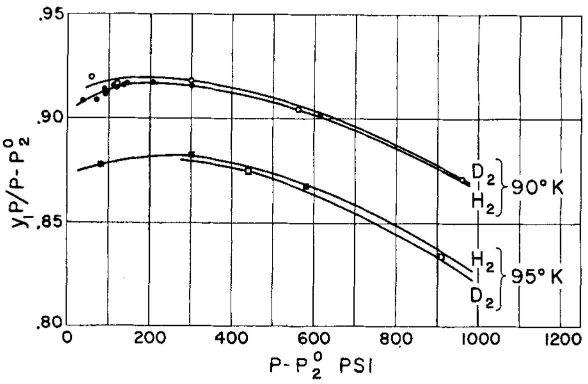

Fig. 4. Hydrogen-nitrogen and deuterium-nitrogen systems: vapor compositions.

When data of high accuracy are plotted, it is preferable to show the deviations from some idealized simple behavior rather than the full range of the data. Examples are the compressibility factor and residual volume ways of expressing PVT data.

For liquid-vapor equilibrium data it is desirable to handle the liquid and vapor compositions independently, to avoid compounding the errors.

LIQUID COMPOSITIONS

One of the common ways of smoothing liquid compositions is to plot the vapor pressure of mixtures of constant composition in a reference-substance type of plot (*12*), but this method is not applicable to systems like the hydrogen-nitrogen system because in this case the lines have slopes very different from those of the reference substance. Thus while the total pressure increases with temperature for pure nitrogen and for mixtures containing less 8% hydrogen, it is practically independent of temperature for mixtures containing 8% hydrogen, and decreases with an increase in temperature for richer mixtures.

The concentration of hydrogen in the liquid increases almost linearly with pressure at constant temperature, indicating that Henry's law should be followed rather closely. Henry's law can be written as

$$x_1 = k\overline{P}_1 \qquad (1)$$

The partial pressure of hydrogen in the vapor can be expressed in terms of the total pressure and the partial pressure of nitrogen as

$$\overline{P}_1 = P - \overline{P}_2 \qquad (2)$$

and if Raoult's law applies to the liquid phase, the partial pressure of nitrogen can be expressed in terms of the liquid composition

$$\overline{P}_2 = P_2^\circ\,(1 - x_1) \qquad (3)$$

One can substitute this value in Equation (1), obtaining

$$x_1 = k\,P - P_2^\circ\,(1 - x_1) \qquad (4)$$

which can be further simplified to

$$x_1 = k'\,(P - P_2^\circ) \qquad (5)$$

which neglects the effect of the liquid composition. From Equation (5) the value of k' is

$$k' = \frac{x_1}{P - P_2^\circ} \qquad (6)$$

The value of k' was used in the plots in preference to the value of k because it is a parameter simpler to calculate, and the ratio k'/k is practically constant at 1.009 throughout the pressure range investigated. The variation of k' with pressure and temperature is shown in Figure 3. It can be seen that the solubility of hydrogen in liquid nitrogen, when expressed as mole fraction per pound per square inch partial pressure, increases with both pressure and temperature. The shaded region around each line (Figure 3) indicates the limits of error in the values of k' corresponding to an error of ± 0.01% in the composition of the liquid phase. The parameter k' was plotted vs. $P - P_2^\circ$ instead of the total pressure P to allow for comparisons of solubility at the same values of partial pressure of hydrogen.

VAPOR COMPOSITIONS

If the vapor phase were an ideal gas mixture, the following relationship would hold:

$$\overline{P}_1 = y_1 P = P - P_2^\circ x_2 \qquad (7)$$

This can be simplified again by neglecting the effect of liquid composition to obtain

$$\overline{P}_1 \cong yP \cong P - P_2^\circ \qquad (8)$$

Figure 4 shows the value of the function $yP/(P - P_2^\circ)$, which differs from 1 even at the lowest pressures and has a strong temperature dependence. It is convenient for smoothing isothermal data however because it varies relatively slowly with pressure, except near the critical point of the mixtures.

COMPARISON WITH LITERATURE VALUES

The vapor-liquid equilibrium for the hydrogen-nitrogen system has been determined by several investigators, and some of their results are compared in Figures 5 and 6. Verschoyle (*18*) used the equilibrium-bomb technique and investigated the vapor-liquid equilibrium between the triple point of nitrogen and 85.7°K.[*] The volume of his equilibrium bomb was only 9 ml., so that appreciable pressure changes must have occurred during the sampling of the vapor. This is confirmed by the very low values of hydrogen concentration in the liquid reported at the lower pressures, as can be seen in Figure 5 which shows his 78.2°K. isotherm. The same effect is noticed in his 85.7°K. isotherm (not shown). His data at higher pressures seem to be fairly reliable.

Ruhemann and Zinn (*16*) report data at 78°, 83°, and 90°K.[*] and pressures up to 50 atm. (735 lb./sq. in. abs.). They used a dynamic method in which a mixture of known composition is cooled to the desired temperature through a long cooling coil, and later the liquid and vapor phases are separated and sampled. Unfortunately their data were not tabulated and had to be read off a very small plot; therefore the following conclusions may be colored by a possible reading error. Their 90°K. isothermal data can be seen to differ appreciably from the rest of the literature values. The same is true of their 78° and 83°K. data (not shown).

Later data taken in the same equipment by Steckel and Zinn (*17*) seem to be of much higher quality although subject to the same possible reading error mentioned above. Steckel and Zinn worked at 90°K, 107.7°, and 109°K. and pressures up to 95 atm. (1,396 lb./sq. in.). Their 90°K. data agree fairly well with the data obtained in this work, especially at the higher pressures. Their 107.7° and 109°K. data are not shown.

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[*] The temperature values mentioned may differ from those cited by the original investigator because they were corrected to be in agreement with the values of vapor pressure of nitrogen given by the National Bureau of Standards tables (*11*).

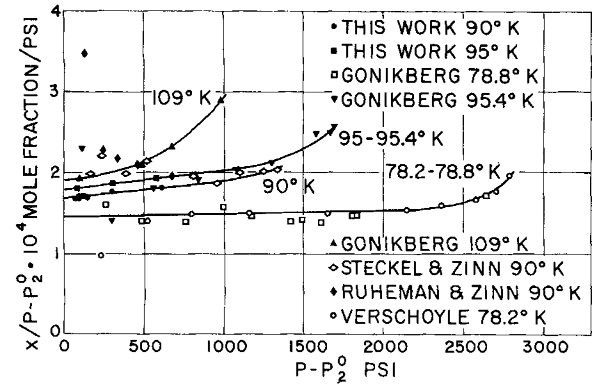

Fig. 5. Hydrogen-nitrogen system: liquid compositions; comparison with literature values.

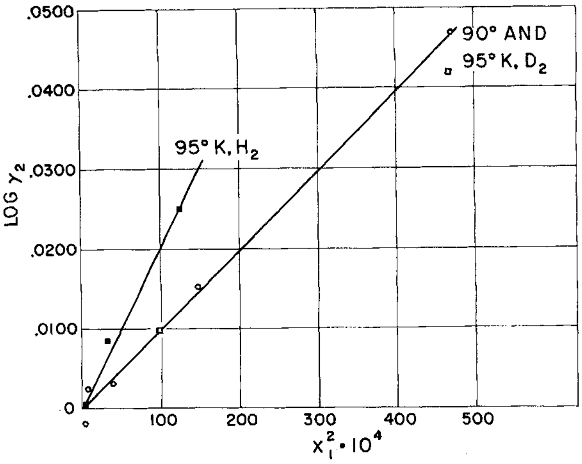

Fig. 7. Activity coefficient of nitrogen in the liquid phase.

Gonickberg and his co-workers (*4*) used the dynamic method in an apparatus very similar to Dodge's (*2*). They tried to duplicate the 78.2° and 85°K. data of Verschoyle and also obtained data at 95.4° and 109°K. There is some question as to the actual temperature levels at which they obtained their data, because they used the vapor pressure of oxygen together with the vapor-pressure equation of Dodge and Davis (*3*) as their temperature reference. When the temperature calculated from the Dodge and Davis equation* is compared with the temperature as calculated from the vapor pressures of nitrogen reported, a small discrepancy exists:

Nominal temperature, (°K.)	Based on oxygen, (°K.)	Based on nitrogen, (°K.)
79.0	78.81	78.96
86.1	86.06	86.17
95.4	95.45	95.37
109.0	108.95	108.46

It is not known whether the above discrepancies point to an error in the National Bureau of Standards tables or to an error in Gonickberg's data. The agreement between Gonickberg's data at 95.4°K. and the data reported in this work at 95.0°K. is fair, considering the slight difference in temperature levels. Most of the discrepancy in the liquid-sample compositions occurs at low pressures, where the effect of errors in the analysis is more pronounced. The vapor compositions at about 600 lb./sq. in. abs. differ by about 1.5%, but the discrepancy is smaller at the lower pressures. Gonickberg's data at 109°K. are also shown in Figures 5 and 6.

TESTING OF THE DATA FOR THERMODYNAMIC CONSISTENCY

Until recently (*7, 1*) there was no good method with which to test binary phase equilibrium data, for the case where one of the components is much above its critical temperature and the vapor phase can not be considered ideal. Thus none of the methods given by Redlich et al. (*14*), Kuo Tsung Yu (*8*), and Othmer (*12, 13*) can be applied.

The data were tested for thermodynamic consistency by two independent methods, which complement each other. Both methods have the same basic limitation, namely the accuracy with which one can predict the thermodynamic properties of the coexisting phases.

The first method examines the dependence of the activity coefficient of one of the components with concentration. While this dependence can take many forms and still be thermodynamically consistent, for simple mixtures of hydrogen-nitrogen, where the components are not associated and no strong specific interactions can be expected, the activity coefficient should be a simple function of concentration, such as

$$\log \gamma_2 = Bx_1^2 \qquad (9)$$

Thus for a simple system it is necessary that the activity coefficient be expressible by Equation (9); it is however not a sufficient condition for thermodynamic consistency.

The activity coefficient of nitrogen in the liquid was calculated by the methods presented by Redlich (*14*), using the equation of state of Redlich and Kwong (*15*) to calculate the deviations from ideal gas behavior and in particular their so-called "adjusted vapor pressure."

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* Corrected to agree with the National Bureau of Standards values of vapor pressure of oxygen.

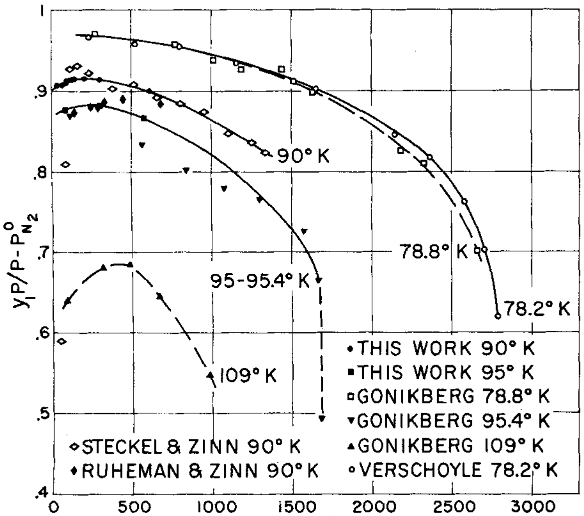

Fig. 6. Hydrogen-nitrogen system: vapor compositions; comparison with literature values.

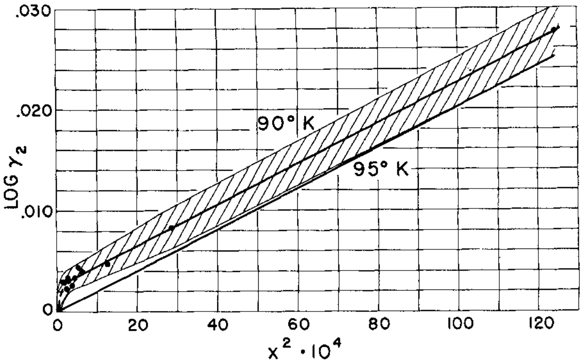

Fig. 8. Hydrogen-nitrogen system; effect of errors in vapor composition on the activity coefficient.

This method of calculating and plotting the data is particularly sensitive to errors in vapor composition because the activity coefficient of nitrogen is obtained from

$$\gamma_2 = \frac{K_2}{Pa/P} = \frac{y_2P}{x_2Pa} \quad (10)$$

and the values of (x_2) are very close to 1, whereas (y_2) is relatively small. Thus any error in the vapor composition has a large effect in log γ_2. Likewise a small error in the temperature at which the data were obtained has a large effect in log γ_2 because it affects directly the values of the adjusted vapor pressure.

Figure 7 shows that indeed the data plot as straight lines. The 90°K. data for the hydrogen-nitrogen system are shown in more detail in Figure 8.

While the line representing the activity coefficients at 95° K. goes through the origin, the line for 90°K. is parallel to it and slightly displaced, but the values at low concentrations indicate a definite curvature towards the origin. Further, Figure 8 shows the range in values of log γ_2 which corresponds to an error of ± 0.1% in vapor composition. This indicates that the vapor compositions are at most 0.2% in error, if one assumes that such a simple equation of state as Redlich and Kwong's together with the approximate integrations used to obtain the adjusted vapor pressure, can be expected to hold within that accuracy.

Using a plot of this type one can easily adjust individual data points and calculate back vapor compositions which are thermodynamically consistent; this is much harder to do with the integral conditions of Alder et al (*1*), which is, for isothermal data, that between any two points *a, b*

$$\int_{f_{1(a)}}^{f_{1(b)}} x_1 d \ln f_1 + \int_{f_{2(a)}}^{f_{2(b)}} x_2 d \ln f_2 = \int_{P(a)}^{P(b)} Z^L \, d \ln P \quad (11)$$

or

$$\int_{K_{1(a)}}^{K_{1(b)}} x_1 \, d \ln K_1 + \int_{K_{2(a)}}^{K_{2(b)}} x_2 \, d \ln K_2 = \int_{P(a)}^{P(b)} [Z^L + Z_1^g y_1(1/K_2 - 1/K_1) - Z^g/K_2] \, d \ln P \quad (12)$$

Equation (11) is rigorous but requires that the liquid volumes be known to a high degree of accuracy; Equation (12) assumes that the Lewis and Randall fugacity rule applies to the vapor but does not require that the liquid volumes be known as accurately.

The data were tested with Equations (11) and (12) and were found to be consistent within the limits of accuracy of the estimates of the different thermodynamic properties. The case of the hydrogen-nitrogen data at 90°K. with Equation (12) will be described in more detail.

The values of Z_1^g and Z^g were estimated with the equation of state of Redlich and Kwong; Z^L was estimated by assuming a linear relation of molar volume with composition and with compressibility corrections by the methods of Lydersen et al. (*9*). The following gives the deviations from Equation (12) for the successive experimental data points:

Run	Patm.	y_1	L.H.S.	R.H.S.	Δ
11-h	6.053	0.3753	—	—	—
11-g	8.325	0.5217	−0.227	−0.226	0.001
18-a	9.935	0.5855	−0.349	−0.346	0.003
11-d	11.188	0.6247	−0.433	−0.425	0.008
11-a	13.389	0.6732	−0.549	−0.539	0.010
10	17.62	0.7324	−0.715	−0.701	0.014
20-a	24.101	0.7800	−0.876	−0.866	0.010
20-b	45.353	0.8304	−1.079	−1.089	−0.010

As could be expected from the calculation method the value of Δ increases as the hydrogen content of the vapor goes through the 50% region, where the deviations from Lewis and Randall fugacity rule and simple additivity of the molar volumes of the individual components is the greatest.

DEUTERIUM

Values of the relative volatility of hydrogen and deuterium in liquid nitrogen were calculated from the smoothed data. The relative volatility at 90°K. is practically constant across pressure at 1.198, decreasing to about 1.196 at 1,000 lb./sq. in. abs., 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 lb./sq. in. abs. is 1.169, while the value at 987.7 lb./sq. in. abs. is 1.185. The average of the two values is 1.177.

ACKNOWLEDGMENT

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NOTATION

B = constant
f = fugacity
K = liquid-vapor equilibrium constant = y/x
k = Henry's law constant
P = pressure
$\overline{P}$ = partial pressure
Pa = adjusted vapor pressure
x = mole fraction in liquid phase
y = mole fraction in vapor phase
Z = compressibility factor = PV/RT
γ = liquid phase activity coefficient

Subscripts

1 = hydrogen or deuterium
2 = nitrogen

Superscripts

o = pure component
g = gas phase
L = liquid phase

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