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NATIONAL BUREAU OF STANDARDS REPORT

3921

LIQUID—VAPOR PHASE EQUILIBRIUM IN SOLUTIONS OF OXYGEN AND NITROGEN AT PRESSURES BELOW ONE ATMOSPHERE

by

George T. Armstrong
Jack M. Goldstein
and
D. Ellis Roberts

Air Research and Development Command Order No. CS 670-53-7

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NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT		NBS REPORT
0305-10-2658	January 31, 1955	3921

Liquid-Vapor Phase Equilibrium in Solutions of Oxygen and Nitrogen at Pressures Below One Atmosphere

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Forward

This is a technical report describing the findings of a project established November 28, 1952, to investigate the properties of mixtures of the components of air. This project was sponsored by the Air Research and Development Command under Order No. CS-670-53-7. It is a continuation of work initiated by the National Advisory Committee for Aeronautics and conducted at the National Bureau of Standards during fiscal year 1952.

The objective of the investigation has been to obtain information concerning the fundamental properties of air and its components, such information being desirable in calculations concerning the design and construction of wind tunnels.

F. G. Brickwedde

F. G. Brickwedde, Chief
Heat and Power Division

Liquid-Vapor Phase Equilibrium in Solutions
of Oxygen and Nitrogen at Pressures Below One Atmosphere

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LIQUID-VAPOR PHASE EQUILIBRIUM IN SOLUTIONS OF OXYGEN AND NITROGEN AT PRESSURES BELOW ONE ATMOSPHERE

ABSTRACT

A cryostat and equilibrium vessel together with auxiliary apparatus for establishing equilibrium between liquid and vapor phases of solutions of low boiling material by a circulation method is described. The equilibrium vessel incorporates a novel liquid sampling device. Vapor and liquid compositions and total vapor pressures of solutions of oxygen and nitrogen were measured along isotherms at 77.5°, 70° and 65°K. The activity coefficients of nitrogen and oxygen may be represented by equations of the form

$\frac{RT}{V_{N_2}} \log_e \gamma_{N_2} = A_{12}\phi^2_{O_2}$ and $\frac{RT}{V_{O_2}} \log_e \gamma_{O_2} = A_{12}\phi^2_{N_2}$, in which A_{12} in cal/cm^3 mole has the values 1.22 at 77.5°, 1.38 at 70° and 1.47 at 65°K. The deviations of the solutions from ideality are much less than is to be expected of regular solutions, in which the interaction energy between unlike molecules follows a geometric mean law. The data are not entirely consistent with the assumption that molar volumes are additive in the solutions. In an appendix a study of the vapor pressure of nitrogen is described.

1. INTRODUCTION

Vapor-liquid equilibrium measurements have been made on the system oxygen-nitrogen over isotherms covering most of the range from 75°K to the critical region. Baly [1][(1)] made measurements by a static method at one atmosphere only. Inglis [2] determined two isotherms, at 74.7°K and 79.07°K by a circulation method. Dodge and Dunbar [3] provided the most complete study of the system, by a circulation method determining isotherms at 90°, 100°, 110°, 120° and 125°. Trapeznikova and Shubnikov [4] determined an isotherm at 85°K. Sagenkahn and Fink [5] made a series of measurements by a static method in the region from one to two atmospheres. The chief interest in this system has been to provide information useful in the separation of air by fractional distillation, and this accounts for the preponderance of measurements at superatmospheric pressures.

(1) Numbers in brackets refer to references at the end of the report.

The production of hypersonic gas velocities in wind tunnels creates temperatures in some cases below 75°K. This development has created an interest in the phase behavior of the components of air at temperatures well below those for which data exist. The present research was undertaken to fill the uncertainties in the liquid region below the normal boiling point of nitrogen.

The possibility that association of oxygen molecules into dimers might occur and cause large deviations from ideality offered an added incentive to undertake the study of this system.

2. EXPERIMENTAL APPARATUS AND PROCEDURES

2.1 The General Experimental Plan

The measurements were made by a circulation method. The vapor mixture from a room temperature reservoir was circulated by a positively acting pump, through the liquid solution in a constant temperature vessel and returned to the room temperature reservoir. Circulation was continued until equilibrium was established; the temperature and pressure were then measured and samples of liquid and vapor were extracted for analysis.

2.2 The Equilibrium Vessel and Cryostat

The equilibrium vessel is protected from external temperatures by two liquid refrigerant baths and an evacuated chamber. The equilibrium vessel is surrounded by a copper can, which can be highly evacuated, or filled with helium for heat transfer. The can not only encloses the vacuum space, but also because of its high thermal conductivity serves to present a uniform temperature environment to the equilibrium vessel. The equilibrium vessel in its thermal shield is immersed in a liquid nitrogen bath. This bath, consisting of a one liter Dewar flask in a covered container suitable for evacuation, is maintained at the desired isothermal temperature and will be called the isothermal bath. The isothermal bath cover is held in place by screws which hold it securely to a heavy flange near the rim of the container. The joint between the cylindrical container and the cover is sealed by a narrow teflon ring gasket. The cover is fitted with a 1/2 in.O.D. thin wall monel tube which serves for filling and also for a vacuum pump connecting tube.

In order to permit maintenance of the isothermal bath at the desired temperature for a reasonable length of time without excessive loss of liquid, it is in turn placed in an outer bath of liquid nitrogen boiling freely at the prevailing atmospheric pressure. A loose fitting lid covers the outer nitrogen bath and at the same time provides support for the isothermal bath which hangs within. Losses of refrigerant from the outer bath are rather rapid, because of the large number of tubes entering it, and because it is necessary to have it filled nearly to the top, so that frequent refilling is necessary.

The inner isothermal bath, protected as it is on all sides by liquid nitrogen, requires much less attention. A filling can be expected to last four hours or longer even when operating at the lowest temperatures. The temperature of the isothermal bath is controlled by regulating the pressure under which the refrigerant (commercial liquid nitrogen) boils. The pressure is reduced by a large vacuum pump, and is maintained near a pre-determined value by a cartesian diver type manostat. The temperature control by this method suffers from two drawbacks. (1) The approach to thermal equilibrium within the isothermal bath is slow, so that a change in the manostat setting is not completely reflected in the temperature of the equilibrium vessel for an hour or more. (2) The constant pumping away of the liquid nitrogen from the isothermal bath continually enriches the residual liquid in oxygen and causes a slow rise of the bath temperature. The effect of the first factor is to require some patience in the establishment of the manostat setting, while the second factor results in the final temperature setting of many of the points lying one or two tenths of a degree above the desired isotherm.

The details of the equilibrium vessel are shown in figure 1. It consists of a copper cylinder D with an inside diameter of one in., an inside height of about three in., and a wall thickness of 1/8 in. The volume of the vessel is about 36 cm^3.

The lid E of the equilibrium vessel is a disc of 1/4 in. brass having a shallow shoulder cut around the rim. This fits a similar shoulder in a flange F on the top of the cylinder. A gasket G of 0.015 in. diameter fine gold wire forms a gas tight joint when the lid is bolted to the flange.

Suspended from the lid is the thermometer well H, a thin walled copper tube, which snugly fits the small platinum resistance thermometer J. Also suspended from the lid is a sheet copper basket K, of semicircular shape, so positioned that the thermometer well passes with a small amount of clearance through a hole in the bottom of the basket. The basket is placed in a position with respect to the vapor lift pump L such that liquid forced by the circulating vapors through the lift pump is caught in the basket and trickles down the thermometer well.

The circulating vapors passing through a quarter inch tube M, enter the vapor lift pump through a T joint at N. The vapor lift pump is the tube M connecting the bottom of the equilibrium vessel to a point in the side wall near the top of the cylinder. The pumping action of the circulating vapors also throughly stirs the liquid in the cylinder of the equilibrium vessel.

Because of the low pressures expected in the equilibrium vessel during many of the measurements, it was not expected that liquid could be effectively removed by suction from the outside. Instead a force pump was incorporated into the equilibrium vessel to apply the necessary pressure to force liquid through a capillary tube to an external sample receiver. The force pump consists of a cup O, of about 1/2 in. diameter in the bottom of the equilibrium vessel, and a close fitting piston P, which can be thrust into the cup by operation from

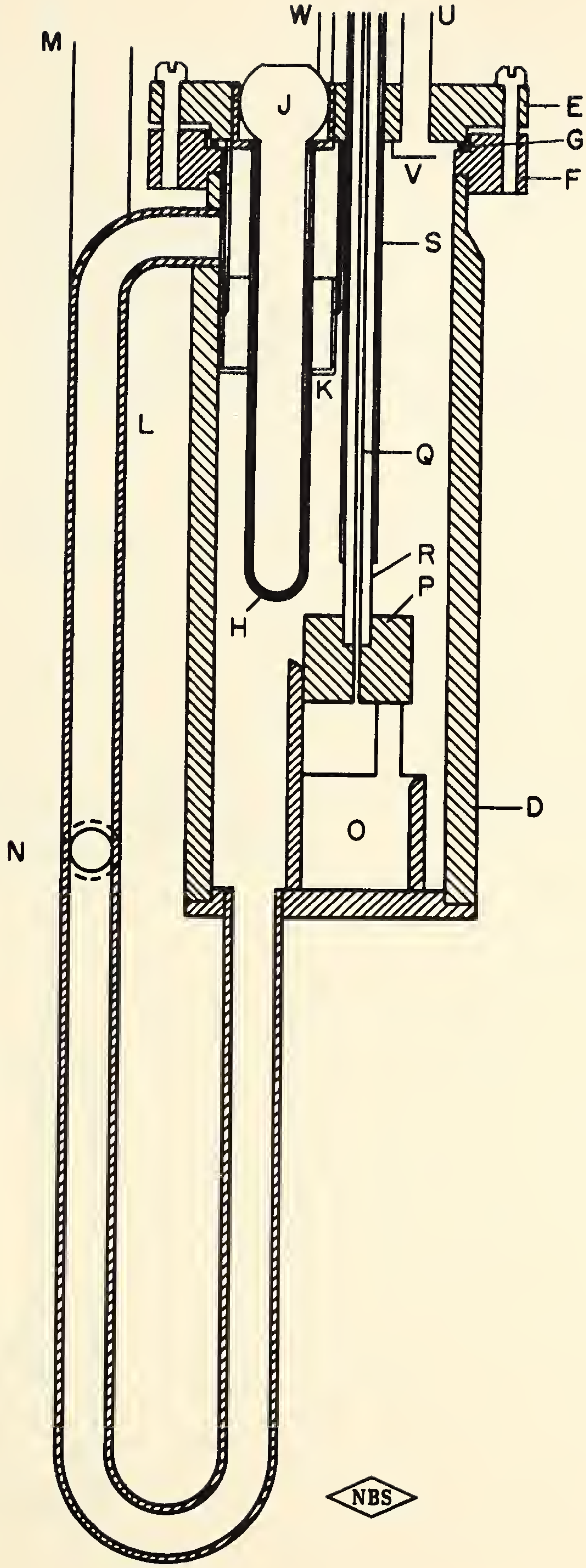


Fig. I. Equilibrium Vessel.

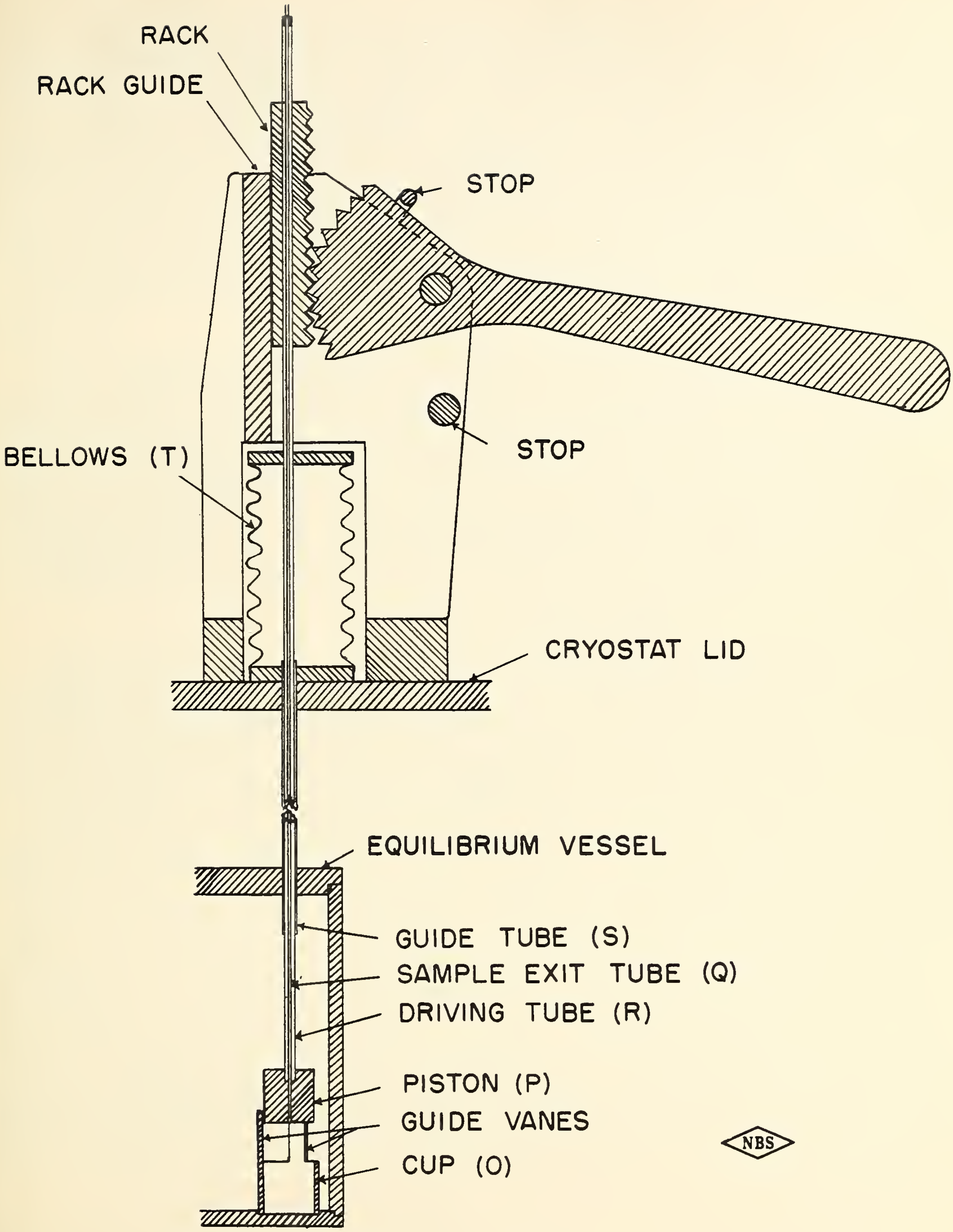


FIG. 2. LIQUID PHASE SAMPLING DEVICE.

outside the cryostat. The liquid trapped in the cup at the time the piston enters it is forced through the small tube Q, having a 1/2 mm. bore, into a mercury filled receiving bulb. During the experiments there was leakage of liquid around the piston but samples obtained were more than adequate in volume for all analyses that were desired. From a cup volume of approximately 1.5 cm^3, a volume of 500 or 600 cm^3 of gas at room temperature and slightly more than atmospheric pressure is delivered in perhaps ten seconds. Figure 2 is a sketch showing the working parts of the sampling device. To force the piston into the cup, a thin wall 1/8 in. monel tube R, guided through the several enclosing chambers by a slightly larger thin wall monel tube S, is driven downward by a manually operated gear and rack. A sylphon bellows T, is used at the top of the cryostat to make a tight closure between the driving tube and the stationary guide tube.

The circulating gas leaves the equilibrium vessel through tube U, which is protected from sprayed droplets by a baffle V, and during part of the experiment was covered with a pad of glass wool. A 1/16 in. diameter tube W leads directly from the equilibrium vessel to the manometer. Electrical leads for the thermometer are brought into the evacuated chamber surrounding the equilibrium vessel via the vacuum pump line, a 1/2 in. thin wall tube, not shown in the diagram, which projects into the evacuated space a short distance. The wires are wrapped several turns around this projecting end to insure their being at the isothermal bath temperature before leading to the thermometer.

2.3 Gas Circulation System

The vapor mixture of oxygen and nitrogen was circulated through the liquid providing an opportunity for equilibrium to be established between the liquid and sufficient vapor for analysis, and at the same time stirring the liquid. The vapor was brought out of the cryostat during a portion of the cycle. It passed through a bulb A (figure 3), which in the 70° and 77.5° measurements had a volume of 500 cm^3, but for the 65° measurements was replaced by a bulb having a volume of 2000 cm^3, in order to provide sufficient vapor phase for analysis. The bulb could be closed off from the circulation line in order to remove a sample of the vapor for analysis. A circulatory pump B, intended to cause movement of the gas without appreciably changing the volume of the system during any portion of its cycle, was used to force the gas mixture along the path from the gas reservoir bulb, into the equilibrium vessel via the vapor lift pump and return it to the gas reservoir bulb. At times a flowmeter, either an oil bubbler, or a spherical ball suspended in a small tube by the gas stream, was inserted in the line to monitor the flow. The circulatory pump used in these experiments was a commercially available flexible liner pump, in which a rotating eccentric cam presses the liner against a plastic enclosing block and by its eccentric motion presses a bubble of gas forward, simultaneously admitting more gas behind the rotating part. By combination of motor shunts and different gear ratios a variety of circulation speeds was available.

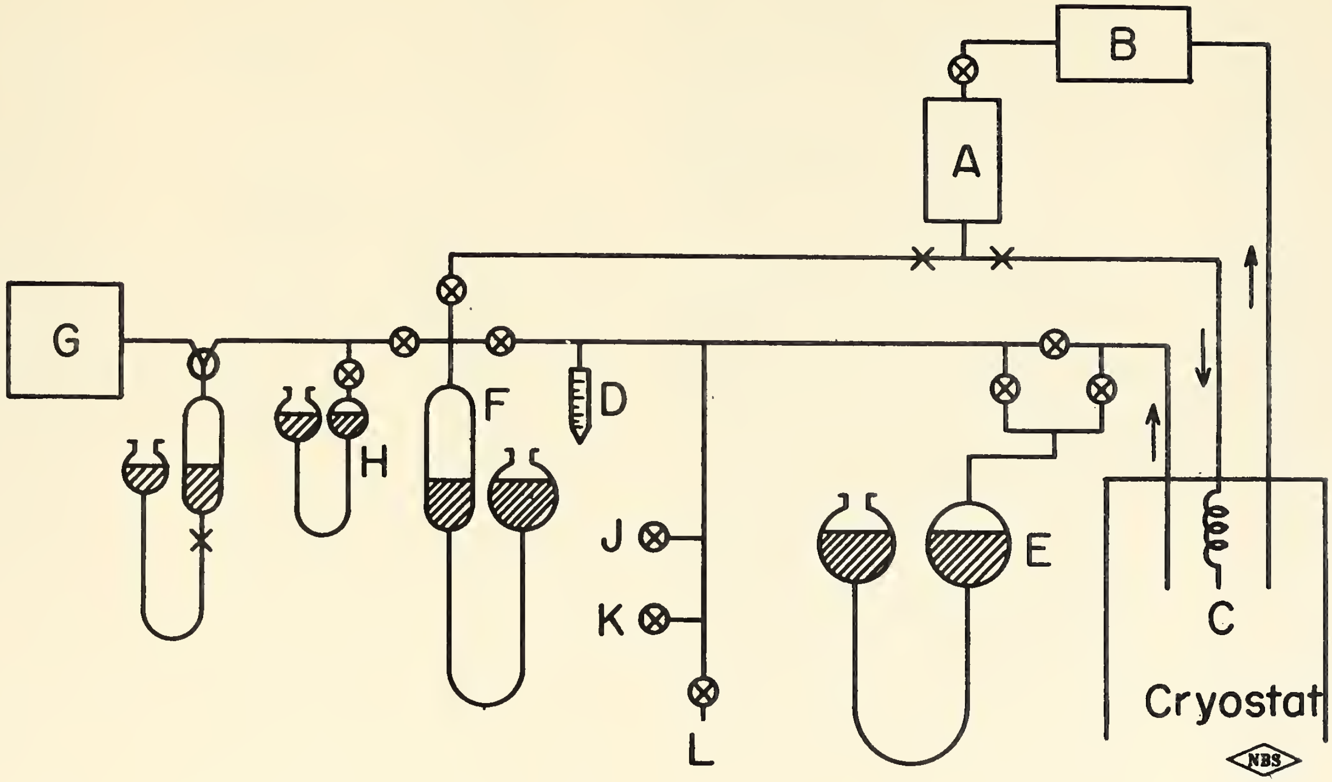


Fig. 3. Gas Handling System.

When first operated with reduced pressure in the equilibrium system the active flexible liner of the circulatory pump collapsed against the enclosing block, thus preventing any pumping action. It was found possible to rectify this situation by modifying the pump slightly to permit a substantially equal vacuum to be placed external to the flexible liner. The circulating action of the pump could thus be maintained down to the lowest pressures encountered. The pump and the gas reservoir bulb were kept in a constant temperature oil bath to prevent changes of pressure due to changes in ambient temperature. This precaution was probably not necessary.

The gases were at room temperature entering the cryostat. It was found that if they were permitted to run directly to the equilibrium vessel a slow rise of the equilibrium vessel temperature occurred as long as circulation continued. A coil C, of a few turns of copper tubing was inserted in the flow line at the point where the gases entered the outermost liquid nitrogen bath. This coil tempered the gases sufficiently well to prevent rising temperatures in the equilibrium vessel due to transport of heat by the gases during circulation. This may be illustrated by the tests at the oxygen point on March 19. The temperature of boiling oxygen was measured to be 89.82° without circulation; with circulation the temperature dropped to 89.77°. The temperature calculated from Hoge's vapor pressure data on oxygen was .0077° higher than the observed temperature without circulation; it was .0025° higher during circulation. After discontinuing the circulation the calculated temperature remained 0.0007° higher than the measured temperature. Similar results were obtained on another test March 26.

2.4 Temperature and Pressure Measurement

The thermometer used in the measurements was a platinum resistance thermometer of the capsule type, calibrated below the oxygen point against the provisional temperature scale established by Hoge and Brickwedde [6] at the National Bureau of Standards.

Pressure measurements were made with a precision manometer in which the positions of the mercury surfaces are located by a micrometer depth gage in conjunction with pointed stainless steel rods of calibrated lengths, and the contacts between the rods and the mercury are detected electrically. This manometer has been described [7] (See appendix). Figure 4 is a picture of the manometer.

2.5 Gas Handling and Analysis

The material to be used in the equilibrium vessel was measured by first condensing to liquid in a graduated tube D (figure 3) of 15 cm^3 capacity. The liquid was then transferred by distillation into the equilibrium vessel by way of the circulatory system. The circulatory pump was usually operated during condensation. Samples of gas from the liquid sample extractor were collected in a 1000 cm^3 bulb, E, which was full of mercury before the sample

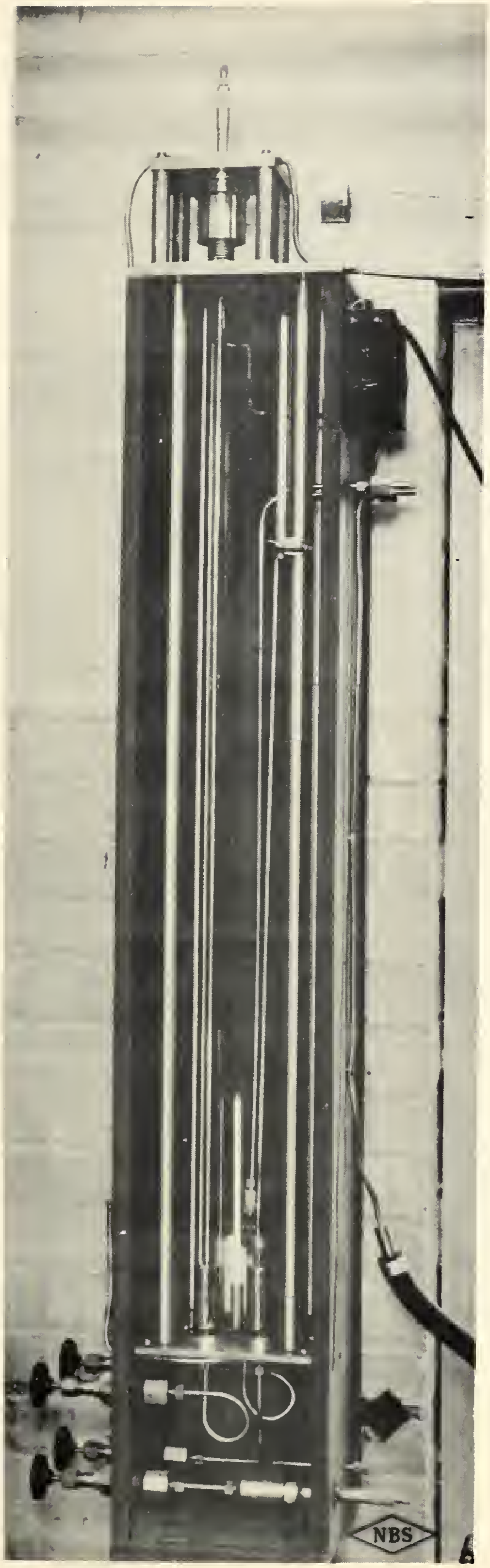


Fig. 4. Precision Manometer

was taken. After the sample was taken the gas was compressed to slightly greater than atmospheric pressure to be retained until time for analysis. A 500 cm^3 bulb F, which could be filled with mercury was used for transferring gas from the storage bulb F or the vapor sample, bulb A to the gas analysis apparatus G. A third auxiliary bulb H, of 200 cm^3, was available to store a sample for later analysis if other bulbs were in use. The pure gases oxygen and nitrogen were introduced at J and K. A vacuum pump connected at L permitted evacuation of the whole gas handling system, or such parts of it as were necessary before transferring gases.

2.6 Analysis of the Liquid and Vapor Samples

A commercial Shepard type volumetric gas analysis apparatus was used for analysis of the samples. Alkaline pyrogallol solutions for the absorption of oxygen were prepared according to the instructions of Kilday [8], to minimize carbon monoxide formation in the analysis of mixtures of high oxygen content. In general two analyses were made of each sample, with the exceptions that in several of the early runs, three or more analyses were made in order to assure reproducibility, and in some of the runs with solutions high in oxygen content at the lower temperatures the vapor sample was insufficient for more than one analysis. For the 907 analyses performed on samples for which more than one analysis was made the mean deviation was ±0.03 mole percent from the mean for the samples.

2.7 Materials Used in the Experiments

Commercially available compressed oxygen and nitrogen were used. The nitrogen was standard high purity dry nitrogen purchased from the Linde Air Products Company. The oxygen was a special high purity grade furnished through the courtesy of the Linde Air Products Company. Both were stated by the supplier to contain less than 0.005 percent of impurities. A study of the vapor pressure of the nitrogen has been previously reported [7]. The oxygen vapor pressure was checked at the normal boiling point and the boiling point agreed to within ±0.005° with the value reported by Hoge [9].

2.8 Experimental Procedure

In preparation for an equilibrium measurement, the equilibrium vessel previously cooled to the desired temperature was filled with approximately 25 cm^3 of oxygen and nitrogen in proportions measured by condensing them separately in the graduated tube D (figure 3) before transfer to the equilibrium vessel. The gas handling system was then closed off from the circulation system. Circulation was maintained from two to four hours at a rate generally about 275 to 300 cm^3 of gas per minute except during certain experiments designed to determine whether variation of the circulating speed affected the measured equilibrium. This rate had been found in earlier tests of the vapor lift pump

to be adequate to operate the pump. These tests had shown that a wide range of liquid levels in the equilibrium vessel and a wide range of vapor circulation rates would maintain action of the lift pump. The long periods of circulation were required by the slow approach of the equilibrium vessel temperature to a steady state.

After the temperature had remained constant to within a few hundredths of a degree for fifteen minutes to half an hour a series of temperature and pressure measurements were made, at two minute intervals, either simultaneously by two observers or on alternate minutes by a single observer. At the conclusion of a third or fourth temperature reading the circulation was stopped, the vapor sample bulb closed off from the rest of the circulation system, and the liquid sample was taken. This total operation including collection of the desired liquid sample was completed generally in less than 1-1/2 minutes.

The procedure for collecting the liquid sample was adopted after several experiments described in a discussion of the results. Equilibrium was established with the piston in the cup. The liquid sample flow line was opened to the vacuum pump. The piston was raised; one liquid sample was expelled into the vacuum system and rejected. Then the liquid sample flow line was opened to the sample collecting bulb, the piston raised again, and a second sample was forced out, into the collecting bulb where it was held for analysis. Analyses were generally performed during the same day the samples were collected, except that the last samples collected one day were sometimes analyzed on the next working day.

3. DISCUSSION OF THE EXPERIMENTAL MEASUREMENTS

The direct results of the experimental measurements are shown in Table 1. Part A is the 77.5° isotherm, part B is the 70° isotherm and part C is the 65° isotherm. Each experimental point is numbered, the numbers running consecutively through all experimental points in the chronological order in which the measurements were made. No points were discarded, although some might have been for valid reasons which will be discussed later.

Of the experimental points, run number 32 is incomplete because the vapor sample was unintentionally discarded. The data observed are shown in columns 2-7, they are the absolute temperature, T; the pressure in atmospheres, P; the mole fractions in the liquid, x_{N_2} and x_{O_2}; and the mole fractions in the vapor, y_{N_2} and y_{O_2}. In column 1 is shown the date of the equilibrium measurement.

The treatment of the data is discussed in a later section; however, it will be helpful for the present to refer to figure 5, showing $\log_e \alpha$ plotted as functions of x_{N_2} for the three isotherms, in the discussion of the experiment which follows. In this figure the run number of each experimental point is shown to permit identification. The measurements represent a wide variety of

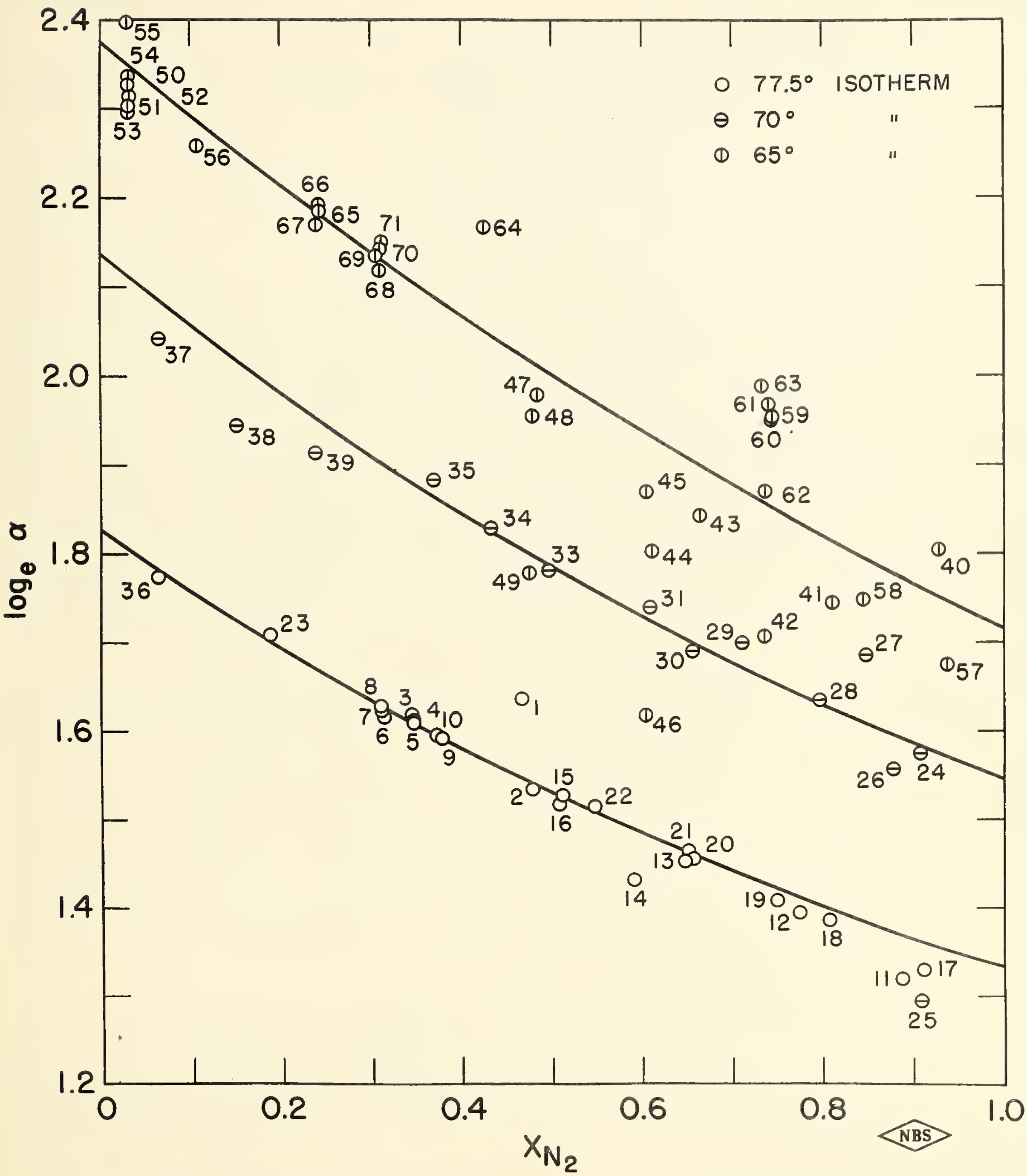


Fig. 5. Logarithm of the separation coefficient for oxygen – nitrogen solutions.

detailed procedures used in bringing the liquid and vapor to equilibrium, and in sampling.

The first ten runs on the 77.5° isotherm represent attempts to learn the reproducibility of successive samples, to determine whether the sampling technique was adequate and to examine the possibility of entrainment of liquid in the vapor. Run number one was made with the sampling piston lifted out of the cup, leaving in the cup an undisturbed volume of liquid which probably did not reach proper equilibrium and which formed the bulk of the first sample. In this run oxygen was added first and would be expected to form a disproportionate amount of the liquid sample. It is therefore justifiable to disregard this run as unsatisfactory in procedure. Run number two made after further circulation of the same liquid gives a value of $\log_e \alpha$ in good agreement with neighboring points. Runs three, four, and five form a series in which after circulating with the piston lowered into the cup, three liquid samples were taken within an hour from the same liquid mixture, and the vapor sample was taken only at the end. Here again oxygen was added first and nitrogen last. Runs six, seven and eight form a similar series, in which one vapor sample and three liquid samples were taken from one liquid mixture; but in this case oxygen was added last. There is an obvious tendency for the points in each series to approach a common line (when plotted as $\log_e \alpha$) and in each case the earliest run differs from later runs in the direction to be expected if the material in the liquid sample was disproportionately rich in the component added to the equilibrium vessel first. Thereupon the obvious course was adopted of discarding the first liquid sample completely and was followed in all later runs.

The possibility of entrainment of liquid in the vapor stream was investigated in the next series of measurements, represented by runs nine and ten. The device used to detect entrainment was the variation of the circulation rate. Run nine was made with the circulating pump operating at full speed until the samples were taken; while in run ten, after full speed circulation of the same mixture for three quarters of an hour the pump was cut to approximately 1/4 speed for 50 minutes. The values of $\log_e \alpha$ obtained from runs nine and ten are in excellent agreement with each other and with the later measurements of all the preceding series. Therefore it was concluded at this point that a suitable sampling procedure had been found and that the samples obtained were satisfactorily reproducible.

In carrying out the remainder of the measurements, it became apparent after a time that overall reproducibility of a point was not as good as had been anticipated. Because of lingering doubts about the possibility of entrainment a pad of glass wool to catch liquid droplets was placed over the vapor outlet tube as early as run 11, and remained there until run 50 at which time it was replaced by a metal baffle.

The data of the 77.5° isotherm form a reasonably smooth pattern of points, the data of the 70° isotherm are somewhat more scattered. The data of the 65° isotherm have become seriously irregular. In the course of the measurements

numerous attempts were made to discover the cause of the irregularities and lack of reproducibility and these will be touched on briefly.

a. No consistent effect on $\log_e \alpha$ could be traced to upward or downward temperature drift of the equilibrium vessel.

b. Repeated checks of the analyses showed that the scatter of the data could not be accounted for on the basis of differences in analysis of several portions of the same sample.

c. No effect could be attributed to the storage of some samples overnight before analysis, or to the storage of a few of the early samples under reduced pressure. All samples made after run 23 were stored under pressure slightly greater than atmospheric until analyzed.

d. The thermal insulating vacuum space around the equilibrium vessel was usually filled with helium during changes of temperature, and was usually filled with helium overnight. Leakage of helium into the equilibrium vessel would result in high apparent values of nitrogen. The residue of an analysis of a sample obtained after the equilibrium vessel had stood overnight surrounded by helium was examined by mass spectrometer. No helium was detected.

e. It was suspected that the fullness of the equilibrium vessel might affect the efficiency of stirring by the circulation. Runs 50 through 55 and 59 through 63 were made without addition of new solution to the equilibrium vessel. In the latter series of runs the volume of solution diminished from 29 cm^3 to 17 cm^3. While there is no question that an effect was produced, and series 50 through 55 seems to follow a cyclic pattern, no basis has been arrived at for concluding that one value was better than another.

f. Examination of the data as a whole reveals two suggestive trends: that the scatter of the points becomes worse as the experiments continue, and that the scatter of points becomes worse the lower is the temperature. Because the data were obtained in order from higher to lower temperature these two trends are impossible to assess separately.

The dependence of the scatter upon time would require a deterioration of the apparatus or an unnoticed change in the experimental procedure. Most parts of the apparatus were checked from time to time during the experiments without any indication of faulty operation. One possible source of difficulty which was not specifically checked is that the leaky joint between the thermometer well and the basket became clogged and failed to allow the mixture to drain through. This would have resulted in a pocket of unstirred liquid which might have contributed erratically to the composition of the mixture.

More likely, however, appears to be the effect of the much lower pressures prevailing at the lower temperatures. The lower pressures would mean that if entrainment of liquid droplets in the vapor stream occurred, a given size drop of liquid would disturb the vapor composition more than at higher pressures.

In another way, too, the lower mass of vapor present at the lower pressures could play a part. In the operation of the vapor lift pump a small pressure differential must build up between the inside and outside of the equilibrium vessel. Some condensation must occur on the high pressure side as a result and some evaporation occurs at the lower pressure surface. If at a low pressure the condensation and evaporation should be sufficient to account for the total mass of gas flowing through the circulating system, stirring of the liquid would cease to be systematic. Although sporadic stirring might occur, the compositions measured would very probably be unreproducible. Evidence for the existence of this behavior was seen in the fluctuations of an auxiliary manometer connected to the flow system, which were obvious at pressures above 250 mm but diminished steadily as the pressure was reduced. These fluctuations were presumably related to the passage of bubbles through the pumping tube. One fact that hinders the above interpretation is the nearly constant spread of values of $\log_e \alpha$ over the whole isotherm, although the vapor pressures of the nitrogen rich solutions are several times those of the oxygen rich solutions. Another corroborative piece of evidence is the cooling effect of the circulation. This might be possible if evaporation were occurring near the thermometer and condensation in the inlet tube rather far separated from the thermometer, with a temperature gradient arising between these two locations. The cooling effect of circulation amounted to several hundredths of a degree. Rough calculations suggest that at a pressure of about 50 mm, total condensation and evaporation from the surface of 300 cm^3 of gas per minute would be sufficient to produce a temperature decrease of 0.05° at the evaporating surface.

4. CALCULATION OF THE DATA

The results of the measurements form three isotherms at 65°, 70° and 77.5°K. Individual points deviate as much as 0.4° from the isotherm, and therefore it was felt to be impractical to adjust one or more of the directly observed variables to find corresponding points exactly on the isotherm. Instead, the activity coefficient γ, or rather its logarithm, was computed for each point. Then the values $\log_e \gamma$, a rather slowly varying function of temperature, were adjusted to bring them to the isotherm. For the calculation of $\log_e \gamma$ the following formula was used for nitrogen.

$$\log_e \gamma_{N_2} = \log_e \frac{P\, y_{N_2}}{P^o_{N_2}} + \log_e \frac{f_{N_2}}{P} - \log_e \frac{f^o_{N_2}}{P^o_{N_2}} - \log_e x_{N_2}$$

In this formula P is the experimental pressure; $P^o_{N_2}$ is the vapor pressure of pure nitrogen at the experimental temperature; y_{N_2} is the mole fraction of nitrogen in the vapor; x_{N_2} is the mole fraction of nitrogen in the liquid; f_{N_2} is the fugacity of nitrogen at pressure P and $f^o_{N_2}$ its fugacity at pressure $P^o_{N_2}$. The term $\log_e \frac{f^o_{N_2}}{P^o_{N_2}}$ is a correction for the nonideality of nitrogen gas

in its pure state at its saturation line; and the term $\log_e \frac{f_{N_2}}{P}$ is a correction for the non-ideality of nitrogen gas in its mixture with oxygen at the experimental pressure. The latter term is derived on the basis of the proposal by Lewis and Randall [10] for the fugacity of a component of a gas mixture.

The fugacity correction term $\log_e \frac{f_{N_2}}{P} - \log_e \frac{f^o_{N_2}}{P^o_{N_2}}$ was approximated by the term $B'_{N_2} (P-P^o_{N_2})$ in which B'_{N_2}, a function of temperature only, is related to the second virial coefficient. Similar formulas were used for the calculation of $\log_e \gamma_{O_2}$. The values previously determined [7] of $\log_e \frac{f^o_{N_2}}{P^o_{N_2}}$ along the saturation line of nitrogen permitted the evaluation of B'_{N_2} as a function of temperature. The values of B'_{O_2} were obtained from a calculation of the second virial coefficient of oxygen, B_{O_2}, by Woolley [11], and the relation $B'_{O_2}=B_{O_2}/RT$. The values of B'_{N_2} and B'_{O_2} at 65°, 70° and 77.5° are shown in Table 3.

For $P^o_{N_2}$ the vapor pressure data of Armstrong [7] were used; and for $P^o_{O_2}$ the vapor pressure data of Hoge [9] were used. These values together with the fugacity correction terms are shown in Table 1. The terms $\log_e a_{N_2}$ and $\log_e a_{O_2}$, in which _a_ is the activity were calculated from the preceding data for each experimental point and are also shown in Table 1. The terms $\log_e \gamma_{N_2}$ and $\log_e \gamma_{O_2}$ for each run at the experimental temperature are shown in Table 2. The $\Delta \log_e \gamma$ terms are the corrections needed to bring the values of $\log_e \gamma$ to the isotherms, and are based on the small shift in $\log_e \gamma$ with temperature. The columns labelled $\log_e \gamma_{N_2}$ (at isotherm) and $\log_e \gamma_{O_2}$ (at isotherm) have been thus corrected for the small temperature difference existing between the observed point and the isotherm and these values are used in subsequent calculations.

For the correlation of the data two functions were considered:

$$\frac{RT}{V_{N_2}} \log_e \gamma_{N_2} = A_{12} \phi_{O_2}^2 \tag{1a}$$

$$\frac{RT}{V_{O_2}} \log_e \gamma_{O_2} = A_{12} \phi_{N_2}^2 \tag{1b}$$

and

$$\frac{RT}{V_{N_2}} \log_e \gamma_{N_2} = \frac{RT}{V_{N_2}} \left[\log_e \frac{\phi_{N_2}}{X_{N_2}} + \phi_{O_2} \left(1 - \frac{V_{N_2}}{V_{O_2}}\right) \right] + A_{12} \phi_{O_2}^2 \tag{2a}$$

$$\frac{RT}{V_{O_2}} \log_e \gamma_{O_2} = \frac{RT}{V_{O_2}} \left[\log_e \frac{\phi_{O_2}}{X_{O_2}} + \phi_{N_2} \left(1 - \frac{V_{O_2}}{V_{N_2}}\right) \right] + A_{12} \phi_{N_2}^2 \tag{2b}$$

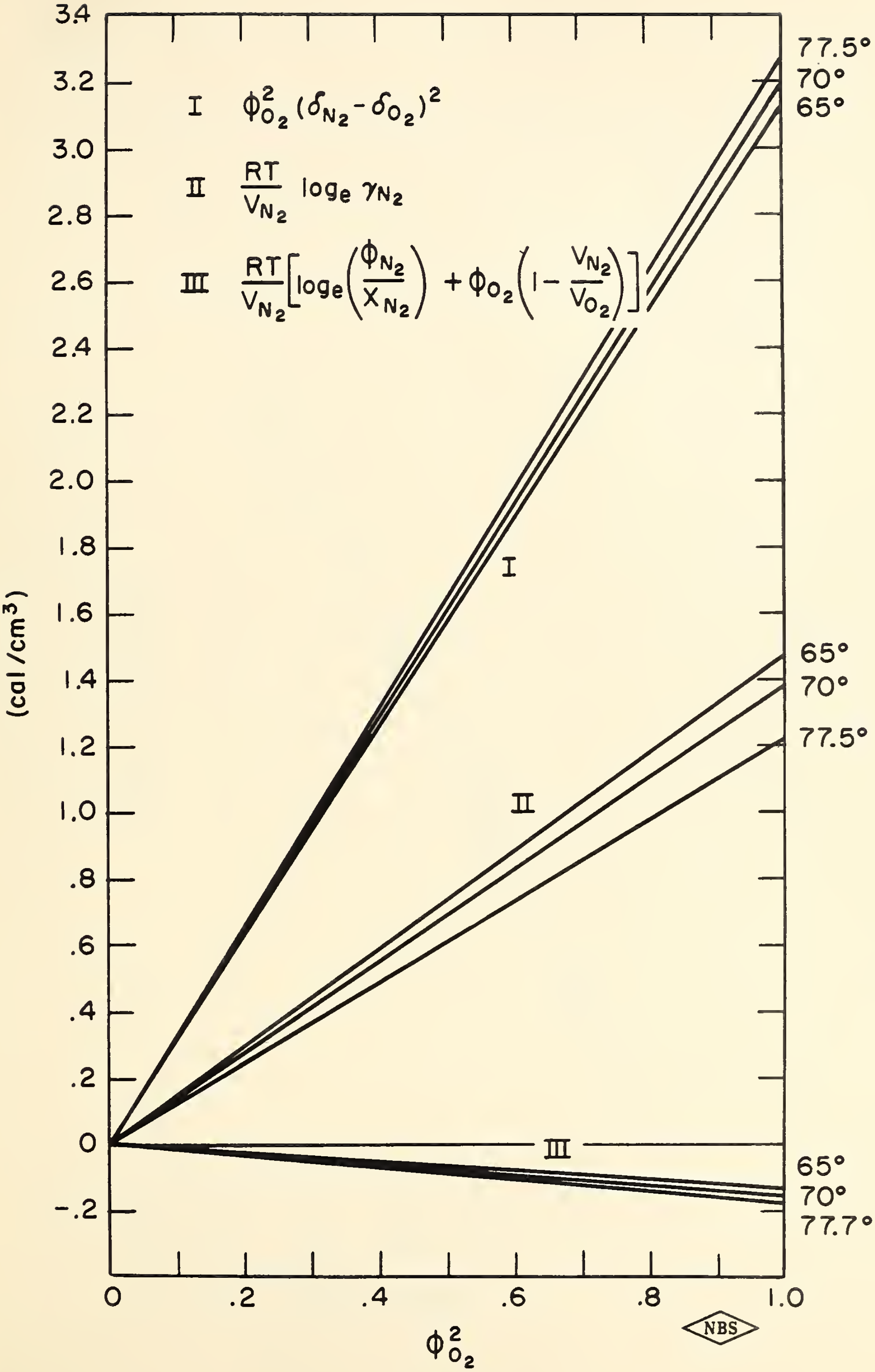
In these equations V_{N_2} and V_{O_2} are the molar volumes respectively of nitrogen and oxygen; ϕ_{N_2} and ϕ_{O_2} are the volume fractions in the solution, $A_{12} = (C_{11} + C_{22} - 2C_{12})$, where C_{11} and C_{22} are the cohesive energy densities of the pure components and C_{12} results from the interaction of the two different molecules.

Equations (1a) and (1b) follow from Hildebrand's criterion of a regular solution, that the entropy of mixing is ideal. The additional terms in equations (2a) and (2b) reflect the probable maximum effect of differences in molecular size on the entropy of mixing.

For the molar volumes required, the data of Baly and Donnan [12] were used for oxygen and the data of Mathias, Onnes and Crommelin [13] were used for nitrogen. The volume fraction in these mixtures is significantly different from the mole fraction as is shown in Table 4 in which are tabulated the volume fractions at uniform intervals of mole fractions for the three isotherms. In this calculation the assumption was made that there is no volume change in mixing.

The terms $\frac{RT}{V_{N_2}}\left[\log_e \frac{\phi_{N_2}}{x_{N_2}} + \phi_{O_2}\left(1 - \frac{V_{N_2}}{V_{O_2}}\right)\right]$ were evaluated at even values of x_{N_2} for the three isotherms, and when plotted against $\phi^2_{O_2}$ are very nearly linear. In figure 6 are shown these functions and also $\phi^2_{O_2}(\delta_{N_2} - \delta_{O_2})^2$. In the latter term $(\delta_{N_2} - \delta_{O_2})^2$ represents the A_{12} of equation (1) and is obtained on the assumption that $C_{12} = C_{11} C_{22}$ and by replacing C_{11} by $\delta^2_{N_2}$ and C_{22} by $\delta^2_{O_2}$.

Thus it appears that if $\frac{RT}{V_{N_2}}\log_e \gamma_{N_2}$ is plotted as a function of $\phi^2_{O_2}$, a linear relation should be obtained if either equations 1 or equations 2 apply to the system. A plot of the data is shown in figures 7, 8 and 9, in which $\frac{RT}{V_{N_2}}\log_e \gamma_{N_2}$ is plotted against $\phi^2_{O_2}$ and on the same scale, by interchanging the variables, $\frac{RT}{V_{O_2}}\log_e \gamma_{O_2}$ is plotted as a function of $\phi^2_{N_2}$. If equations (1) apply, the data should fall on a single straight line for each isotherm. It is seen that there is a reasonably good fit, with a fairly definite tendency for $\frac{RT}{V_{O_2}}\log_e \gamma_{O_2}$ to lie somewhat above $\frac{RT}{V_{N_2}}\log_e \gamma_{N_2}$ in the region of large ϕ_{N_2}. In passing a line through the data, rather large weight was given to the values of $\frac{RT}{V_{N_2}}\log_e \gamma_{N_2}$ because these points show very much less scatter than do the $\frac{RT}{V_{O_2}}\log_e \gamma_{O_2}$ points.



3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
0
-.2
(cal/cm³)
I $\phi_{O_2}^2(\delta_{N_2}-\delta_{O_2})^2$
II $\frac{RT}{V_{N_2}}\log_e \gamma_{N_2}$
III $\frac{RT}{V_{N_2}}\left[\log_e\left(\frac{\phi_{N_2}}{X_{N_2}}\right)+\phi_{O_2}\left(1-\frac{V_{N_2}}{V_{O_2}}\right)\right]$
77.5°
70°
65°
I
65°
70°
77.5°
II
III
65°
70°
77.7°
0
.2
.4
.6
.8
1.0
$\phi_{O_2}^2$
NBS

Fig. 6

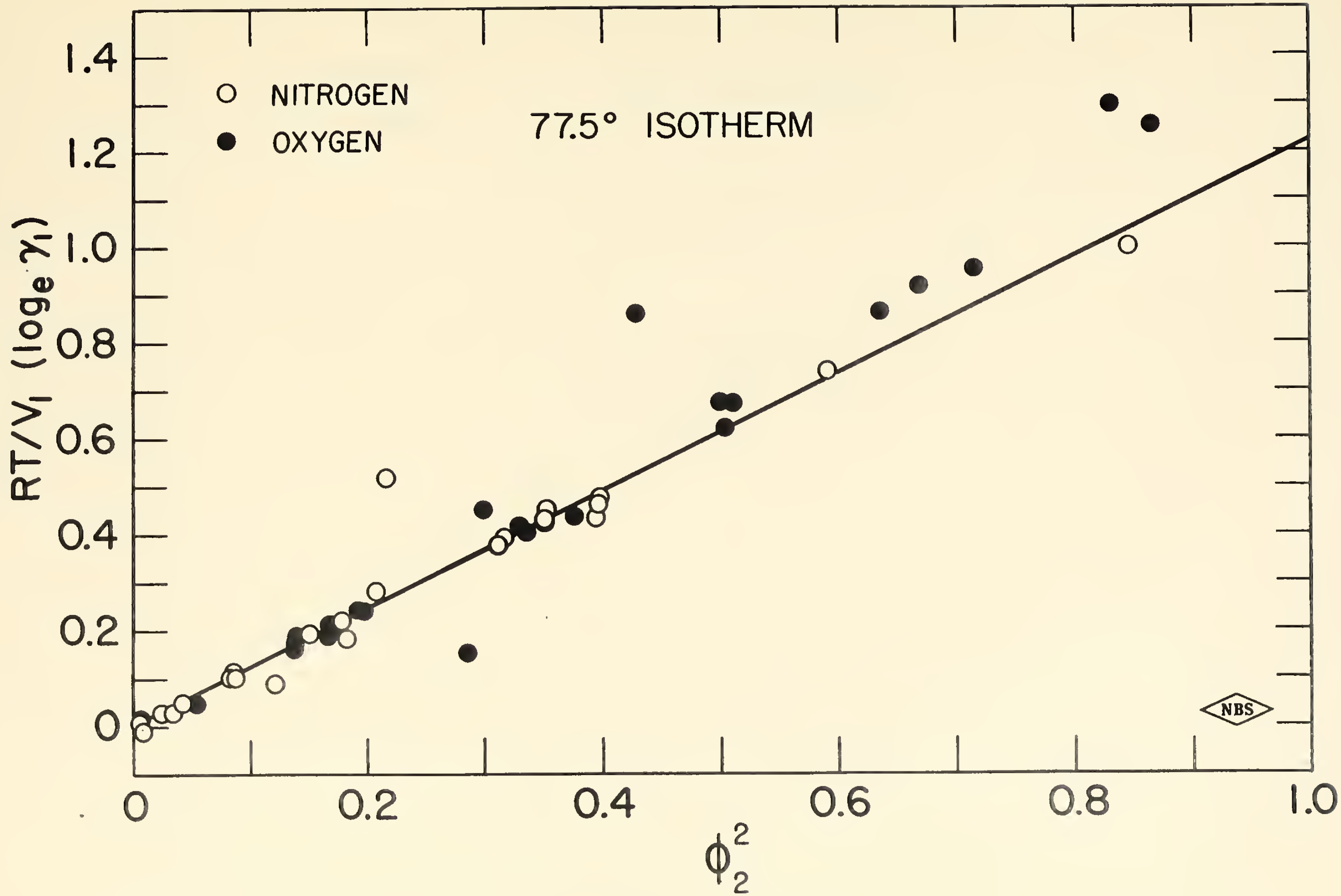


Fig. 7. Oxygen - nitrogen solutions.

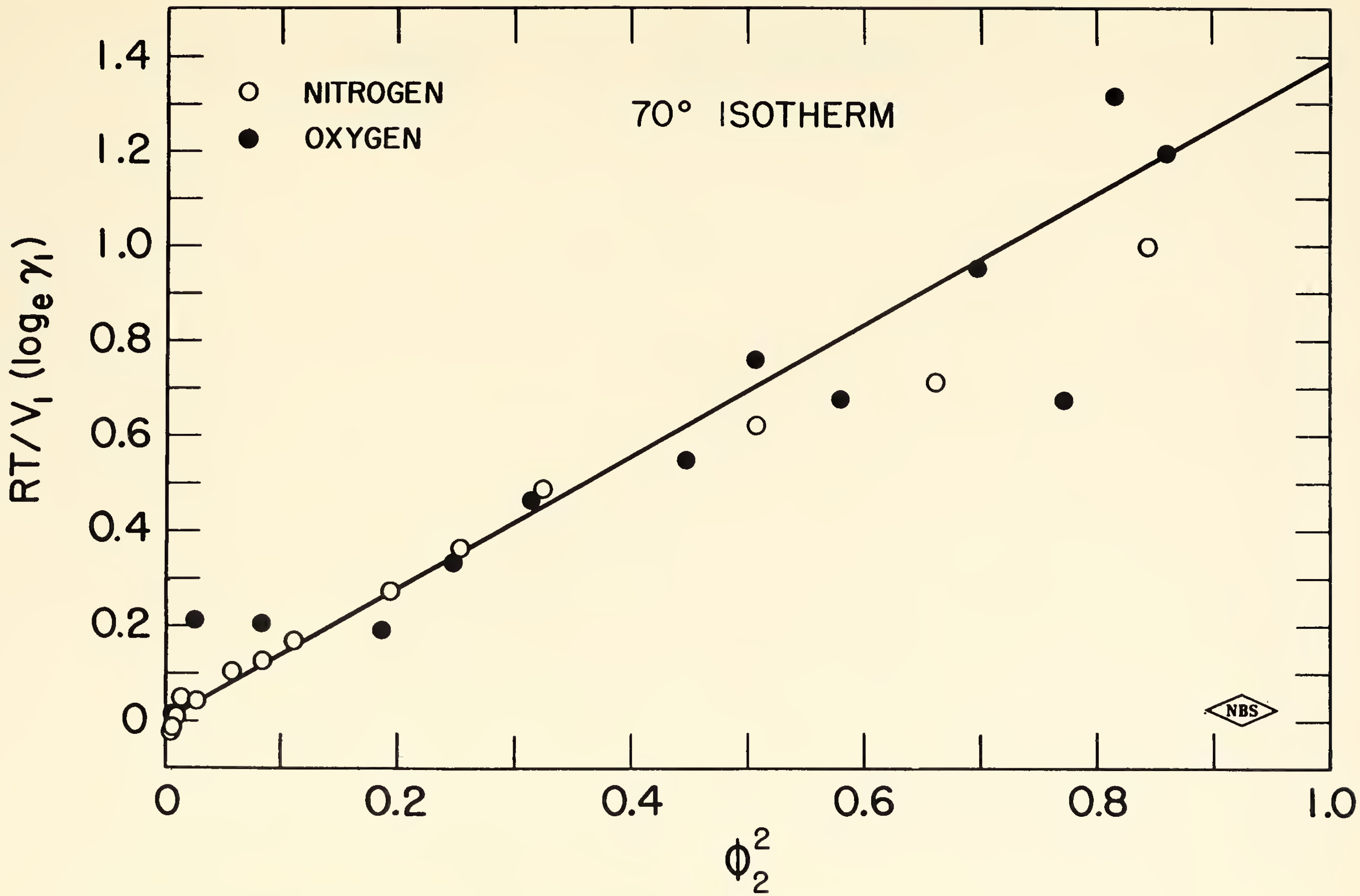


Fig. 8. Oxygen - nitrogen solutions.

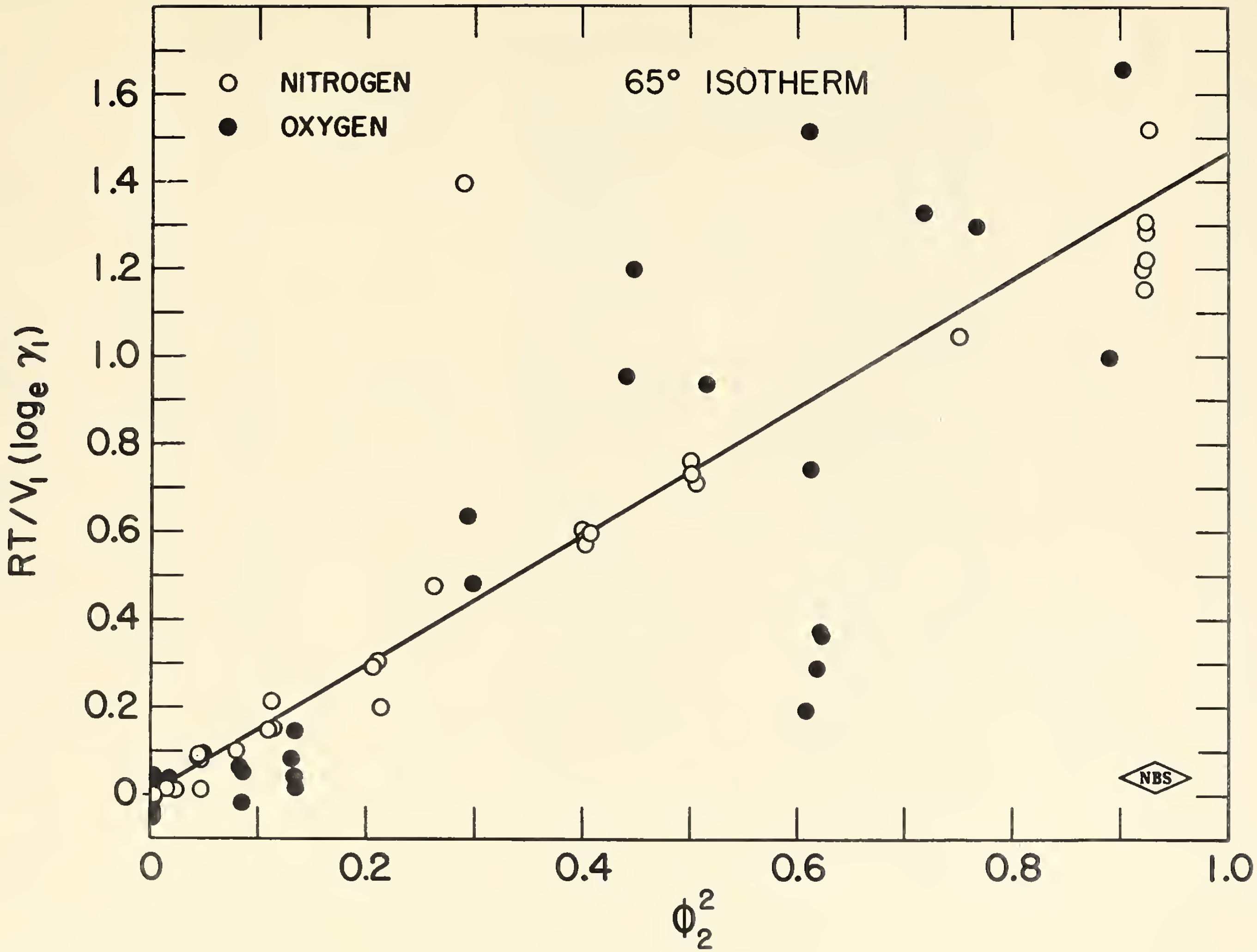


Fig. 9. Oxygen – nitrogen solutions.

The separation coefficient $\alpha = \dfrac{y_{N_2}/y_{O_2}}{x_{N_2}/x_{O_2}}$ was also calculated for each experimental point and is shown in column 9 of Table 1. $\log_e \alpha$ is related to $\log_e \gamma_{N_2}$ and $\log_e \gamma_{O_2}$ by equation (3)

$$\log_e \gamma_{N_2}/\gamma_{O_2} = \log_e \alpha + \log_e P^o_{O_2} - \log_e P^o_{N_2} + B'_{N_2}(P - P^o_{N_2}) - B'_{O_2}(P - P^o_{O_2}) \quad (3)$$

If $\log_e \gamma_{N_2}$ and $\log_e \gamma_{O_2}$ are replaced by $V_{N_2}\left(\frac{A_{12}}{RT}\right)\phi^2_{O_2}$ and $V_{O_2}\left(\frac{A_{12}}{RT}\right)\phi^2_{N_2}$,

then it is possible to devise a smooth function for $\log_e \alpha$ for each isotherm, which is consistent with the activity data. The smooth functions $\log_e \alpha$ are shown in Figure 5 as the solid lines. The variation of $\log_e \alpha$ with temperature can be used to bring exactly to the isotherm the values of $\log_e \alpha$ calculated at the experimental temperatures, and this has been done, assuming for this purpose that over the range of the temperature correction $\log_e \alpha$ varies linearly with temperature. The corrections were made at constant ϕ_{N_2}. The change in x_{N_2} at constant ϕ_{N_2} is less than 0.0002 for the largest corrections in temperatures that were made, and so changes in X_{N_2} have not been made. The corrected values of $\log_e \alpha$ are shown in Figure 5, plotted against the mole fractions of nitrogen in the liquid. It will be noted that in this graph there is a tendency for the data at the extreme ends to fall below the solid curves, suggesting that a straighter line would fit somewhat better. The tendency to fall below is perhaps related to the tendency of the values of $\frac{RT}{V_{O_2}} \log_e \gamma_{O_2}$ to lie above the fitted lines in the plot against $\phi^2_{N_2}$. However, no straight line function of $\frac{RT}{V_1} \log_e \gamma_1$ against ϕ^2_2 can be devised which will cause $\log_e \alpha$ to fit the data at both ends.

The calculation of the equilibrium vapor composition for a given liquid composition can easily be made using the smooth values of $\log_e \alpha$. It is also then possible to calculate the partial pressure of each component and the total vapor pressure of the solution for any value of y_{N_2} or x_{N_2} using the smoothed values of $\log_e \gamma_{N_2}$ in equation (4) and $\log_e \gamma_{O_2}$ in a similar equation.

$$\log_e \gamma_{N_2} = \log_e P + \log_e y_{N_2} + \log_e (f/P)_{N_2} - \log_e P^o_{N_2} - \log_e \left(f^o/P^o\right)_{N_2} - \log_e x_{N_2} \quad (4)$$

5. CALCULATION OF COHESIVE ENERGY DENSITIES FOR OXYGEN AND NITROGEN

Following Hildebrand and Scott [14], consider the cohesive energy density C_{11} to be $-\frac{E}{V_\ell}$ where V_ℓ is the molar volume of the liquid and E is the energy required to evaporate one mole of liquid to vapor at zero pressure. E may be obtained from the heat of vaporization by the following relation

$-E = \left[\Delta H_{vap.} - P(V_g - V_\ell)\right] \frac{V_g}{V_g - V_\ell}$ in which $\Delta H_{vap.}$ is the latent heat of vaporization to the vapor at saturation pressure P, and V_g is the molar volume of vapor. The factor $\frac{V_g}{V_g - V_\ell}$ is required to account for the energy change on reducing the pressure of the vapor to zero. For this calculation of -E we were able to use recent values for the ΔH_{vap} of oxygen determined by Furukawa and McCoskey [15]. The values used are shown in the second column of Table 5. The corresponding vapor pressures for oxygen, shown in the third column, were taken from Hoge [9] and those for nitrogen were calculated from the equation given by Armstrong [7]. Vapor volumes were calculated from the same vapor pressure sources by the use of the relation

$(V_g - V_\ell) = \Delta H_{vap}/T \frac{dP}{dT}$. As also elsewhere in this work the liquid volumes of oxygen were determined from the values reported by Baly and Donnan [12], and those of nitrogen were determined from the values reported by Mathias, Onnes and Crommelin (13). The cohesive energy density is shown in the ninth column of Table 5; and its square root, the solubility parameter δ, is shown in the last column. The solubility parameter for nitrogen, δ_{N_2}, is a linear function of temperature and may be represented by equation (5)

$$\delta_{N_2} = 8.7516 - 0.03720T \qquad (5)$$

with a difference no greater than .001 from the tabulated values of δ. The solubility parameter for oxygen, δ_{O_2}, is nearly linear with temperature, but a small deviation, which will be called Δ, is noticeable. Values of δ_{O_2} may be interpolated using equation (6) in

$$\delta_{O_2} = 10.3666 - 0.03476T + \Delta \qquad (6)$$

(Δ is zero at 68.40° and 91.30°K and has the values + 0.0052 at 76.00° and + 0.0047 at 84.10°K)

which the value of Δ may be selected with sufficient accuracy from a smooth curve drawn through the points noted with the equation.

6. COMPARISON OF EXPERIMENTAL AND THEORETICAL RESULTS

Using the values of δ_{O_2} and δ_{N_2} calculated in section 5, the terms $\phi_{O_2}^2 (\delta_{N_2} - \delta_{O_2})^2$ have been calculated for the three isotherms and are shown as the group I of lines in Figure 6. For comparison the terms $\frac{RT}{V_{N_2}} \log_e \gamma_{N_2}$ obtained from the experimental data are also shown as group II of lines. Group II lines are the term $\frac{RT}{V_{N_2}} \left[\log_e \frac{\Phi_{N_2}}{x_{N_2}} + \phi_{O_2} (1 - \frac{V_{N_2}}{V_{O_2}}) \right]$. It is seen that they are very small compared to either of the other functions or to the difference between them and so will not be considered further. The intercepts of the group I lines at $\phi_{O_2}^2 = 1$ are the experimental values of A_{12} for the three temperatures. If A_{12} were a true constant the isotherms would be superimposed in this plot; but as it is there is a slight increase of A_{12} as the temperature is reduced. One assumption made in deriving the theoretical function $\frac{RT}{V_{N_2}} \log_e \gamma_{N_2} = \phi_{O_2}^2 (\delta_{N_2} - \delta_{O_2})^2$ is that the term C_{12} is the geometric mean of C_{11} and C_{22}. The constant A_{12} becomes $(\delta_{N_2} - \delta_{O_2})^2$ and its value at 77.5° becomes 3.27 cal/cm^3 as compared to 1.22 cal/cm^3 derived from the experimental data. An assumption that $C_{12} = \frac{C_{11} + C_{22}}{2}$ would lead to $A_{12} = 0$. Thus the conclusion seems justified that the interaction energies between unlike molecules lie somewhere between the arithmetic and geometric mean of the interactions between like molecules of the two species. Table 6 shows C_{11} and C_{22} at the three isotherms, evaluated by interpolation from the figures in Table 5, and the value of C_{12} calculated from the experiments and compared with $(C_{11} C_{22})^{1/2}$ and $1/2(C_{11} + C_{22})$. In this Table subscript 1 refers to nitrogen and subscript 2 refers to oxygen.

The solutions of oxygen and nitrogen, when corrected for the non-ideal behavior of the vapors, are considerably more nearly ideal than would be predicted on the basis of the geometric mean hypothesis of interactions. Any possible tendency of oxygen to form dimers at low temperatures would result in

positive deviations from Raoult's law. Because the deviations observed are extremely small, and are much smaller than might be expected even in the absence of such dimerization, it seems unreasonable to attribute any of the observed solution properties to such behavior.

When a plot is made, as in figures 7, 8, and 9, of $\frac{RT}{V_1} \log_e \gamma_1$ against volume fraction of component 2, the nitrogen activity data at the 77.5° isotherm appears to form a good straight line, but the oxygen activities tend to curve upward. On the other hand when plotted against mole fraction squared, the $\log_e \gamma_{N_2}$ curves definitely upward and $\log_e \gamma_{O_2}$ curves downward. This suggests that while the volume fraction is a more accurate guide to the solution behavior, the solutions behave as though the molar volumes in solution are more nearly equal than would be expected from the molar volumes of the pure components.

A similar interpretation appears to be suggested by the plots of $\log_e a$ against x_{N_2}. Here, if the molar volumes were equal, a straight line would be expected, as contrasted with the curved line calculated on the basis of the different molar volumes of the pure components. There is a definite tendency, as noted in Section 4, for the experimental points at the extreme ends to fall below the solid curves, suggesting that straight lines would fit the data almost as well as the curved lines shown.

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Table 1.

Run	Date	T°K (observed)	P(atm)	x_{N_2}	x_{O_2}	y_{N_2}	y_{O_2}	α	$\log_e \alpha$ (at T obs)	$P^o_{N_2}$(atm) (at T obs)	$P^o_{O_2}$(atm) (at T obs)	$B'_{N_2}(P-P^o_{N_2})$	$B'_{O_2}(P-P^o_{O_2})$	$\log_e a_{N_2}$ (at T obs)	$\log_e a_{O_2}$ (at T obs)
Part A 77.5 Isotherm															
1	April 15	77.9428	0.67729	0.4670	0.5330	0.8165	0.1835	5.077	1.624	1.06987	0.22232	+0.0148	-0.0221	-0.6451	-0.6037
2		77.8503	.65792	.4789	.5211	.8082	.1918	4.586	1.523	1.05851	.21942	.0152	- .0213	- .6733	- .5745
3	April 20	77.7305	.53891	.3446	.6554	.7248	.2752	5.008	1.611	1.04382	.21562	.0193	- .0158	- .9637	- .3900
4		77.7129	.53755	.3461	.6539	.7248	.2752	4.975	1.604	1.04168	.21508	.0193	- .0157	- .9641	- .3899
5		77.6749	.53499	.3462	.6538	.7248	.2752	4.975	1.604	1.03707	.21389	.0192	- .0157	- .9646	- .3892
6	April 21	77.7450	.50950	.3128	.6872	.6945	.3055	4.993	1.608	1.04558	.21607	.0205	- .0143	-1.0630	- .3423
7		77.761	.51022	.3113	.6887	.6945	.3055	5.029	1.615	1.04753	.21657	.0205	- .0143	-1.0634	- .3432
8		77.765	.51037	.3103	.6897	.6945	.3055	5.053	1.620	1.04800	.21671	.0205	- .0143	-1.0636	- .3435
9	April 23	77.7256	.56364	.3782	.6218	.7480	.2520	4.880	1.585	1.04322	.21547	.0183	- .0170	-0.8877	- .4337
10		77.7925	.56543	.3735	.6265	.7444	.2556	4.885	1.586	1.05139	.21757	.0186	- .0170	- .8968	- .4260
11	April 27	77.4185	.91829	.8875	.1125	.9673	.0327	3.750	1.322	1.00642	.20606	.0034	- .0350	- .1215	-1.9610
12		77.3534	.82865	.7738	.2262	.9327	.0673	4.050	1.399	0.99875	.20408	.0067	- .0308	- .2497	-1.3281
13		77.5388	.75479	.6478	.3522	.8871	.1129	4.270	1.452	1.02072	.20970	.0103	- .0269	- .4113	-0.9274
14	April 29	77.2694	.68718	.5906	.4094	.8572	.1428	4.160	1.426	0.98891	.20159	.0118	- .0241	- .5063	- .7441
15	April 30	77.6315	.66096	.5119	.4881	.8280	.1720	4.591	1.524	1.03184	.21257	.0142	- .0220	- .6200	- .6478
16		77.6254	.65199	.5073	.4927	.8238	.1762	4.541	1.513	1.03112	.21237	.0145	- .0215	- .6377	- .6359
17	May 3	77.5463	.95303	.9104	.0896	.9746	.0254	3.778	1.329	1.02161	.20993	.0026	- .0365	- .0926	-2.1967
18	May 4	77.7410	.89492	.8070	.1930	.9433	.0567	3.978	1.381	1.04511	.21596	.0057	- .0331	- .2078	-1.4815
19	May 5	77.5113	.82861	.7499	.2501	.9246	.0754	4.090	1.409	1.01743	.20887	.0073	- .0304	- .2764	-1.2373
20		77.5014	.75813	.6563	.3437	.8911	.1089	4.287	1.456	1.01626	.20858	.0100	- .0270	- .3983	- .9520
21		77.4755	.75271	.6511	.3489	.8899	.1101	4.331	1.466	1.02240	.20778	.0104	- .0268	- .4034	- .9459
22	May 6	77.5168	.67928	.5477	.4523	.8464	.1536	4.549	1.515	1.01809	.20903	.0131	- .0231	- .5583	- .7179
23	May 7	77.4172	.38793	.1875	.8125	.5610	.4390	5.538	1.712	1.00605	.20601	.0239	- .0090	-1.5071	- .1994
36	May 31	77.5600	.27691	.0632	.9368	.2841	.7159	5.882	1.772	1.02327	.21037	.0287	- .0033	-2.5368	- .0627

Run	Date	T^oK (observed)	P(atm)	x_{N_2}	x_{O_2}	y_{N_2}	y_{O_2}	α	$\log_e \alpha$ (at T obs)	$P^o_{N_2}$(atm) (at T obs)	$P^o_{O_2}$(atm) (at T obs)	$B'_{N_2}(P-P^o_{N_2})$	$B'_{O_2}(P-P^o_{O_2})$	$\log_e a_{N_2}$ (at T obs)	$\log_e a_{O_2}$ (at T obs)
								Part B	70^o Isotherm						
24	May 14	69.7383	0.33732	0.9074	0.0926	.9795	0.0205	4.874	1.584	0.36591	0.05864	+0.0016	−0.0189	−0.1005	−2.1566
25		70.2718	.36663	.9084	.0916	.9729	.0271	3.619	1.286	.39566	.06474	.0015	− .0200	− .1022	−1.8943
26	May 17	70.1258	.34989	.8774	.1226	.9713	.0287	4.729	1.554	.38733	.06298	.0020	− .0191	− .1288	−1.8551
27	May 24	70.3268	.35274	.8479	.1521	.9675	.0325	5.339	1.675	.39883	.06534	.0025	− .0189	− .1534	−1.7593
28	May 25	70.3058	.33499	.7967	.2033	.9521	.0479	5.072	1.624	.39763	.06504	.0033	− .0178	− .2172	−1.4174
29		70.2062	.30578	.7117	.2883	.9307	.0693	5.441	1.694	.39190	.06386	.0046	− .0160	− .3154	−1.1191
30	May 26	70.1427	.28628	.6560	.3440	.9114	.0886	5.392	1.685	.38829	.06313	.0055	− .0148	− .3922	−0.9267
31		70.2323	.27588	.6090	.3904	.8982	.1018	5.648	1.731	.39339	.06414	.0063	− .0140	− .4559	− .8400
32	May 27	70.2590	.26103	Discarded		.8270	.1730	−	−	.39492	.06460	.0071	− .0130	− .5969	− .3710
33		70.2631	.24328	.4961	.5031	.8528	.1472	5.876	1.771	.39514	.06460	.0081	− .0118	− .6362	− .6017
34	May 28	70.2310	.22291	.4325	.5675	.8246	.1754	6.171	1.820	.39332	.06414	.0091	− .0105	− .7516	− .5056
35		70.3027	.20605	.3694	.6306	.7921	.2079	6.504	1.872	.39743	.06504	.0102	− .0093	− .8798	− .4269
37	June 1	69.9039	.08695	.0643	.9357	.3471	.6529	7.736	2.046	.37495	.06042	.0156	− .0018	−2.5040	− .0641
38		70.0302	.12237	.1509	.8491	.5510	.4490	6.904	1.932	.38196	.06197	.0140	− .0040	−1.7203	− .1243
39	June 2	69.9396	.15130	.2381	.7619	.6799	.3201	6.798	1.917	.37692	.06084	.0122	− .0061	−1.2863	− .2341
								Part C	65^o Isotherm						
40	June 7	65.0858	0.16359	0.9282	0.0718	0.9874	0.0126	6.063	1.802	0.17420	0.02334	+0.0006	−0.0117	−0.0750	−2.4388
41	June 8	64.9475	.14371	.8112	.1888	.9610	.0390	5.736	1.747	.17010	.02266	.0017	− .0102	− .2066	−1.4070
42		65.0300	.13533	.7357	.2643	.9388	.0612	5.509	1.706	.17009	.02308	.0022	− .0094	− .3038	−1.0341
43		65.1480	.12916	.6644	.3356	.9255	.0745	6.275	1.837	.17608	.02367	.0030	− .0088	− .3843	−0.9089
44	June 9	65.1997	.13079	.6111	.3889	.9044	.0956	6.021	1.795	.17764	.02395	.0030	− .0089	− .4553	− .7102
45		65.1115	.12266	.6057	.3943	.9084	.0916	6.457	1.865	.17497	.02345	.0034	− .0083	− .4479	− .7441
46		65.0595	.12261	.6041	.3959	.8848	.1152	5.034	1.616	.17341	.02324	.0033	− .0083	− .4658	− .5062
47	June 10	65.2654	.10686	.4834	.5166	.8702	.1298	7.163	1.969	.17966	.02428	.0047	− .0069	− .6539	− .5667
48	June 11	65.1311	.10433	.4789	.5211	.8659	.1341	7.027	1.950	.17557	.02357	.0046	− .0067	− .6599	− .5279
49		65.2347	.10554	.4748	.5252	.8413	.1587	5.864	1.769	.17872	.02411	.0047	− .0068	− .6948	− .3710
50	June 15	64.8358	.02876	.0312	.9688	.2496	.7504	10.327	2.335	.16683	.02214	.0090	− .0006	−3.1370	− .0263

Table 1 (Continued - 2)

Run	Date	T^oK (observed)	P(atm)	x_{N_2}	x_{O_2}	y_{N_2}	y_{O_2}	α	$\log_e\alpha$ (at T obs)	$P^o_{N_2}$(atm) (at T obs)	$P^o_{O_2}$(atm) (at T obs)	$B'_{N_2}(P-P^o_{N_2})$	$B'_{O_2}(P-P^o_{O_2})$	$\log_e a_{N_2}$ (at T obs)	$\log_e a_{O_2}$ (at T obs)
51		64.8623	0.02876	0.0310	0.9690	0.2437	0.7563	10.071	2.310	0.16761	0.02224	+0.0090	-0.0006	-3.1654	-0.0229
52	June 16	65.2375	.03086	.0323	.9677	.2505	.7495	10.012	2.304	.17880	.02411	.0095	- .0006	-3.1319	- .0423
53		65.1427	.03013	.0312	.9688	.2412	.7588	9.871	2.290	.17592	.02362	.0094	- .0005	-3.1772	- .0328
54		65.2942	.02978	.0309	.9691	.2452	.7548	10.187	2.321	.18055	.02439	.0096	- .0004	-3.1551	- .0389
55	June 17	65.4351	.03218	.0299	.9701	.2489	.7511	10.751	2.375	.18493	.02513	.0097	- .0006	-3.1294	- .0393
56	June 18	65.3413	.04741	.1073	.8927	.5311	.4689	9.423	2.243	.18201	.02467	.0086	- .0019	-1.9695	- .1062
57	June 22	65.2718	.17028	.9368	.0632	.9874	.0126	5.286	1.665	.17986	.02428	.0006	- .0121	-0.0668	-2.4382
58		65.2116	.15558	.8452	.1548	.9689	.0311	5.704	1.741	.17801	.02400	.0014	- .0109	- .1648	-1.6123
59	June 23	65.0456	.13793	.7447	.2553	.9536	.0464	7.050	1.953	.17300	.02313	.0023	- .0096	- .2718	-1.2945
60		65.1846	.14108	.7442	.2558	.9531	.0469	6.989	1.944	.17718	.02383	.0023	- .0098	- .2737	-1.2914
61		65.2281	.14168	.7412	.2588	.9531	.0469	7.097	1.960	.17851	.02405	.0024	- .0098	- .2767	-1.2963
62	June 24	64.9488	.13457	.7365	.2635	.9482	.0518	6.508	1.873	.17013	.02266	.0022	- .0094	- .2855	-1.1881
63	June 25	65.0762	.13675	.7334	.2666	.9525	.0475	7.289	1.986	.17392	.02329	.0024	- .0095	- .2867	-1.2865
64		65.3343	.10025	.4252	.5748	.8644	.1356	8.618	2.154	.18179	.02462	.0052	- .0063	- .7358	-0.6000
65	June 28	64.9460	.06712	.2431	.7569	.7411	.2589	8.913	2.188	.17005	.02266	.0067	- .0037	-1.2225	- .2690
66	June 29	65.2510	.07013	.2424	.7576	.7389	.2611	8.845	2.180	.17921	.02417	.0070	- .0038	-1.2337	- .2811
67		65.1719	.06866	.2396	.7604	.7324	.2676	8.687	2.162	.17680	.02378	.0069	- .0037	-1.2504	- .2616
68		65.2816	.08124	.3092	.6908	.7862	.2138	8.216	2.106	.18016	.02433	.0063	- .0047	-1.0307	- .3419
69	June 30	65.2642	.08055	.3057	.6943	.7865	.2135	8.367	2.124	.17962	.02428	.0063	- .0047	-1.0358	- .3494
70		65.3517	.08225	.3098	.6902	.7899	.2101	8.377	2.126	.18230	.02472	.0064	- .0048	-1.0256	- .3632
71		65.4031	.08345	.3113	.6887	.7925	.2075	8.450	2.134	.18393	.02496	.0064	- .0048	-1.0165	- .3703

Table 2.

Run	$\log_e x_{N_2}$	$\log_e x_{O_2}$	$\log_e \gamma_{N_2}$ (at T obs)	$\log_e \gamma_{O_2}$ (at T obs)	ΔT	$\Delta \log_e \gamma_{N_2}$	$\Delta \log_e \gamma_{O_2}$	$\Delta \log_e \alpha$	$\log_e \gamma_{N_2}$ at isotherm	$\log_e \gamma_{O_2}$ at isotherm	$\log_e \alpha$ at isotherm	$\frac{RT}{V_{N_2}} \log_e \gamma_{N_2}$	$\frac{RT}{V_{O_2}} \log_e \gamma_{O_2}$	$\phi^2_{N_2}$	$\phi^2_{O_2}$
								Part A 77.5° Isotherm							
1	-0.7614	-0.6292	0.1163	0.0255	-0.4428	+0.0006	0.0006	0.013	0.1169	0.0261	1.637	0.518	0.151	0.2848	0.2174
2	- .7362	- .6518	.0629	.0773	- .3808	.0005	.0006	.011	.0634	.0779	1.534	.281	.451	.2977	.2065
3	-1.0654	- .4225	.1017	.0325	- .2305	.0005	.0002	.007	.1022	.0327	1.618	.453	.189	.1658	.3514
4	-1.0610	- .4248	.0969	.0349	- .2129	.0005	.0002	.007	.0974	.0351	1.611	.432	.203	.1672	.3494
5	-1.0607	- .4249	.0961	.0357	- .1749	.0004	.0002	.005	.0965	.0359	1.609	.428	.208	.1673	.3493
6	-1.1622	- .3751	.0992	.0328	- .2450	.0006	.0002	.008	.0998	.0330	1.616	.443	.191	.1391	.3933
7	-1.1670	- .3730	.1036	.0298	- .261	.0006	.0002	.008	.1042	.0300	1.623	.462	.174	.1378	.3954
8	-1.1702	- .3715	.1066	.0280	- .265	.0007	.0002	.008	.1073	.0282	1.628	.476	.163	.1370	.3968
9	-0.9723	- .4751	.0846	.0414	- .2256	.0004	.0002	.007	.0850	.0416	1.592	.377	.241	.1961	.3105
10	- .9848	- .4676	.0880	.0416	- .2925	.0006	.0003	.009	.0886	.0419	1.595	.393	.243	.1918	.3160
11	- .1194	-2.1848	-.0021	.2238	+ .0815	.0000	-.0003	-.002	-.0021	.2235	1.320	-.009	1.295	.8306	.0078
12	- .2564	-1.4863	+.0067	.1588	.1466	.0000	-.0005	-.004	.0067	.1583	1.395	+.030	0.917	.6680	.0334
13	- .4342	-1.0436	.0229	.1162	- .0388	.0000	+.0001	+.001	.0229	.1163	1.453	.102	.674	.4986	.0864
14	- .5266	-0.8931	.0203	.1490	+ .2306	-.0002	-.0005	.006	.0201	.1485	1.432	.089	.860	.4271	.1201
15	- .6696	- .7172	.0496	.0694	- .1315	+.0001	+.0002	.004	.0497	.0696	1.528	.220	.403	.3342	.1780
16	- .6786	- .7078	.0409	.0719	- .1254	.0001	.0002	.004	.0410	.0721	1.517	.182	.418	.3289	.1819
17	- .0939	-2.4129	.0013	.2162	- .0463	.0000	.0002	.001	.0013	.2164	1.330	.006	1.254	.8643	.0049
18	- .2144	-1.6451	.0066	.1636	- .2410	.0000	.0009	.006	.0066	.1645	1.387	.029	0.953	.7145	.0239
19	- .2878	-1.3859	.0114	.1486	- .0113	.0000	.0000	.000	.0114	.1486	1.409	.051	.861	.6346	.0414
20	- .4211	-1.0680	.0228	.1160	- .0014	.0000	.0000	.000	.0228	.1160	1.456	.101	.672	.5094	.0820
21	- .4291	-1.0530	.0257	.1071	+ .0245	.0000	-.0001	-.001	.0257	.1070	1.465	.114	.620	.5027	.0847
22	- .6020	-0.7934	.0437	.0755	- .0168	.0000	.0000	.000	.0437	.0755	1.515	.194	.437	.3755	.1499
23	-1.6740	- .2076	.1669	.0082	+ .0828	-.0003	.0000	-.003	.1666	.0082	1.709	.739	.048	.0537	.5903
36	-2.7615	- .0653	.2247	.0026	- .0600	+.0003	.0000	+.002	.2250	.0026	1.774	.998	.015	.0065	.8453

Table 2 (continued 1)

Run	$\log_e x_{N_2}$	$\log_e x_{O_2}$	$\log_e \gamma_{N_2}$ (at T obs)	$\log_e \gamma_{O_2}$ (at T obs)	ΔT	$\Delta \log_e \gamma_{N_2}$	$\Delta \log_e \gamma_{O_2}$	$\Delta \log_e \alpha$	$\log_e \gamma_{N_2}$ at isotherm	$\log_e \gamma_{O_2}$ at isotherm	$\log_e \alpha$ at isotherm	$\frac{RT}{V_{N_2}} \log_e \gamma_{N_2}$	$\frac{RT}{V_{O_2}} \log_e \gamma_{O_2}$	$\phi^2_{N_2}$	$\phi^2_{O_2}$
						Part B 70° Isotherm									
24	-0.0971	-2.3794	-0.0034	0.2228	+0.2617	-0.0000	-0.0012	-0.009	-0.0034	0.2216	1.575	-0.014	1.194	0.8591	0.0053
25	- .0961	-2.3903	- .0061	.4960	- .2718	.0000	+ .0012	+ .009	- .0061	.4972	1.295	- .025	2.678	.8606	.0052
26	- .1308	-2.0988	+ .0020	.2437	- .1258	.0000	.0005	.004	+ .0020	.2442	1.558	+ .008	1.316	.8145	.0095
27	- .1650	-1.8832	.0116	.1239	- .3268	.0000	.0013	.011	.0116	.1252	1.686	.048	0.674	.7714	.0148
28	- .2273	-1.5931	.0101	.1757	- .3058	+ .0001	.0011	.011	.0102	.1768	1.635	.042	.952	.6977	.0271
29	- .3401	-1.2437	.0247	.1246	- .2062	.0001	.0006	.007	.0248	.1252	1.701	.103	.674	.5797	.0569
30	- .4216	-1.0671	.0294	.1404	- .1427	.0001	.0004	.005	.0295	.1408	1.690	.123	.758	.5062	.0832
31	- .4959	-0.9406	.0400	.1006	- .2323	.0002	.0005	.009	.0402	.1011	1.740	.167	.545	.4465	.1101
32	-	-	-	-	- .2590	-	-	-	-	-	-	-	-	-	-
33	- .7010	- .6870	.0648	.0853	- .2631	.0003	.0004	.010	.0651	.0857	1.781	.271	.462	.3138	.1934
34	- .8382	- .5665	.0866	.0609	- .2310	.0004	.0003	.009	.0870	.0612	1.829	.362	.330	.2466	.2534
35	- .9959	- .4611	.1161	.0342	- .3027	.0006	.0003	.012	.1167	.0345	1.884	.486	.186	.1860	.3234
37	-2.7442	- .0665	.2402	.0024	+ .0961	- .0005	.0000	- .004	.2397	.0024	2.042	.998	.013	.0066	.8438
38	-1.8911	- .1636	.1708	.0393	- .0302	+ .0001	.0000	+ .013	.1709	.0393	1.945	.712	.212	.0349	.6615
39	-1.4351	- .2719	.1488	.0378	+ .0604	- .0002	.0000	- .003	.1486	.0378	1.914	.619	.204	.0829	.5070
						Part C 65° Isotherm									
40	-0.0745	-2.6339	-0.0005	0.1951	-0.0858	+0.0000	+0.0004	+0.003	-0.0005	0.1955	1.805	- .002	.997	.8896	.0032
41	- .2092	-1.6671	+ .0026	.2601	+ .0525	.0000	- .0002	- .002	+ .0026	.2599	1.745	+ .010	1.326	.7171	.0235
42	- .3069	-1.3307	.0031	.2966	- .0300	.0000	+ .0001	+ .001	.0031	.2967	1.707	.012	1.514	.6112	.0476
43	- .4095	-1.0918	.0252	.1829	- .1480	+ .0001	.0004	.006	.0253	.1833	1.843	.100	0.935	.5157	.0795
44	- .4924	-0.9444	.0371	.2342	- .1997	.0001	.0005	.008	.0372	.2347	1.803	.147	1.197	.4476	.1096
45	- .5014	- .9306	.0535	.1864	- .1115	.0001	.0003	.005	.0536	.1867	1.870	.213	0.953	.4409	.1129
46	- .5040	- .9266	.0382	.4204	- .0595	.0000	.0001	.002	.0382	.4205	1.618	.151	2.145	.4389	.1139
47	- .7269	- .6605	.0730	.0938	- .2654	.0003	.0004	.011	.0733	.0942	1.980	.291	0.481	.2986	.2058
48	- .7363	- .6518	.0764	.1239	- .1311	.0002	.0002	.006	.0766	.1241	1.956	.304	.633	.2937	.2099
49	- .7448	- .6440	.0500	.2730	- .2347	.0003	.0003	.010	.0503	.2733	1.779	.199	1.394	.2892	.2136
50	-3.4673	- .0317	.3303	.0054	+ .1642	- .0009	.0000	- .008	.3294	.0054	2.327	1.306	0.028	.0015	.9229

Table 2. (continued 2)

Run	$\log_e x_{N_2}$	$\log_e x_{O_2}$	$\log_e \gamma_{N_2}$ (at T obs)	$\log_e \gamma_{O_2}$ (at T obs)	ΔT	$\Delta \log_e \gamma_{N_2}$	$\Delta \log_e \gamma_{O_2}$	$\Delta \log_e \alpha$	$\log_e \gamma_{N_2}$ at isotherm	$\log_e \gamma_{O_2}$ at isotherm	$\log_e \alpha$ at isotherm	$\frac{RT}{\bar{V}_{N_2}} \log_e \gamma_{N_2}$	$\frac{RT}{\bar{V}_{O_2}} \log_e \gamma_{O_2}$	$\phi^2_{N_2}$	$\phi^2_{O_2}$
51	-3.4738	-0.0315	+0.3084	+0.0086	+0.1377	-0.0008	0.0000	-0.007	0.3076	+0.0086	2.303	1.220	0.044	0.0015	0.9235
52	-3.4327	- .0328	.3008	- .0095	- .2375	+ .0014	.0000	+ .012	.3022	- .0095	2.316	1.198	- .048	.0017	.9203
53	-3.4673	- .0317	.2901	- .0011	- .1427	.0008	.0000	.007	.2909	- .0011	2.297	1.153	- .006	.0015	.9229
54	-3.4770	- .0314	.3219	- .0075	- .2942	.0017	.0000	.015	.3236	- .0075	2.336	1.283	- .038	.0015	.9237
55	-3.5099	- .0297	.3805	- .0096	- .4351	.0025	.0000	.022	.3830	- .0096	2.397	1.519	- .049	.0014	.9262
56	-2.2321	- .1134	.2626	+ .0072	- .3413	.0016	.0000	.016	.2642	+ .0072	2.259	1.048	+ .037	.0179	.7505
57	-0.0653	-2.7614	- .0015	.3232	- .2718	.0000	.0013	.010	- .0015	.3245	1.675	-0.006	1.656	.9027	.0025
58	- .1681	-1.8656	+ .0033	.2533	- .2116	.0000	.0008	.008	+ .0033	.2541	1.749	+ .013	1.296	.7665	.0155
59	- .2948	-1.3653	.0230	.0708	- .0456	.0000	.0001	.002	.0230	.0709	1.955	.091	0.362	.6234	.0043
60	- .2954	-1.3654	.0217	.0720	- .1846	.0001	.0006	.007	.0218	.0726	1.951	.086	.370	.6228	.0444
61	- .2995	-1.3517	.0228	.0554	- .2281	.0001	.0007	.009	.0229	.0561	1.969	.091	.286	.6187	.0455
62	- .3059	-1.3337	.0204	.1456	+ .0512	.0000	- .0002	- .002	.0204	.1454	1.871	.081	.742	.6128	.0472
63	- .3101	-1.3220	.0234	.0355	- .0762	.0000	+ .0002	+ .003	.0234	.0357	1.989	.093	.182	.6081	.0485
64	- .8552	-0.5537	.1194	- .0463	- .3343	+ .0005	.0004	.014	.1199	- .0459	2.168	.475	- .234	.2379	.2623
65	-1.4143	- .2785	.1915	+ .0095	+ .0540	- .0002	.0000	- .002	.1916	+ .0095	2.186	.760	+ .048	.0855	.5007
66	-1.4172	- .2776	.1835	- .0035	- .2510	+ .0008	.0001	+ .012	.1843	- .0034	2.192	.731	- .017	.0850	.5018
67	-1.4288	- .2739	.1784	+ .0123	- .1719	.0005	.0001	.008	.1789	+ .0124	2.170	.709	+ .063	.0832	.5064
68	-1.1738	- .3699	.1431	.0280	- .2816	.0007	.0002	.013	.1438	.0282	2.119	.570	.144	.1334	.4028
69	-1.1851	- .3648	.1493	.0154	- .2642	.0007	.0002	.012	.1500	.0156	2.136	.595	.080	.1306	.4078
70	-1.1718	- .3708	.1462	.0076	- .3517	.0009	.0002	.016	.1471	.0078	2.142	.583	.040	.1339	.4021
71	-1.1670	- .3730	.1505	.0027	- .4031	.0010	.0003	.018	.1515	.0030	2.152	.601	.015	.1351	.4001

Table 3.

The Terms B'_{N_2} and B'_{O_2}

T °K	B'_{N_2} atm^{-1}	B'_{O_2} atm^{-1}
65	-.0646	-.0839
70	-.0539	-.0669
77.5	-.0385	-.0491

Table 4.

Liquid Oxygen and Nitrogen Molar Volumes and Volume Fractions

	T = 77.5°K		T = 70°K		T = 65°K	
x_{N_2}	V cm^3	ϕ_{N_2}	V cm^3	ϕ_{N_2}	V cm^3	ϕ_{N_2}
0.0	26.58	0.0000	25.82	0.0000	25.32	0.0000
.1	27.40	.1268	26.58	.1257	26.05	.1251
.2	28.21	.2462	27.34	.2443	26.77	.2434
.3	29.03	.3589	28.09	.3567	27.50	.3554
.4	29.84	.4655	28.85	.4631	28.22	.4618
.5	30.66	.5664	29.61	.5640	28.95	.5627
.6	31.47	.6622	30.37	.6599	29.68	.6586
.7	32.29	.7530	31.13	.7510	30.40	.7502
.8	33.10	.8394	31.88	.8381	31.13	.8373
.9	33.92	.9216	32.64	.9210	31.85	.9206
1.0	34.73	1.0000	33.40	1.0000	32.58	1.0000

Table 5.

Cohesive energy densities of oxygen and nitrogen

T °K	ΔH_v cal. $mole^{-1}$	P mm Hg	V_g cm^3	V_l cm^3	$\Delta H \frac{V_g}{V_g - V_l}$ cal. $mole^{-1}$	PV_g cal. $mole^{-1}$	-E cal. $mole^{-1}$	$\frac{-E}{V_l}$ cal. $mole^{-1}$ cm^{-3}	δ
Oxygen									
68.40	1773.0	34.70	1.228×10^5	25.66	1773.4	135.8	1637.6	63.82	7.989
76.00	1727.6	126.74	3.707×10^4	26.42	1728.8	149.7	1579.1	59.77	7.731
84.10	1674.2	381.6	1.344×10^4	27.30	1677.7	163.4	1514.3	55.47	7.448
91.30	1622.9	852.3	6.420×10^3	28.12	1630.0	175.2	1454.8	51.74	7.193
Nitrogen									
68.00	1409.9	213.54	1.954×10^4	33.05	1412.3	132.9	1279.4	38.71	6.222
73.10	1370.7	445.77	9.945×10^3	33.92	1375.4	141.3	1234.1	36.38	6.032
77.364	1336.8	760.00	6.100×10^3	34.70	1344.4	147.7	1196.7	34.49	5.873
78.00	1331.7	818.48	5.700×10^3	34.81	1339.9	148.7	1191.2	34.22	5.850

Table 6.

Experimental and theoretical interaction energies of oxygen and nitrogen

($cal.cm^{-3}$)

T	C_{11}(a)	C_{22}	$(\delta_1 - \delta_2)^2$	A_{12}(expt)	C_{12}(expt)	$(C_{11}C_{22})^{1/2}$	$1/2(C_{11}+C_{22})$
65°	40.12	65.69	3.14	1.47	52.17	51.34	52.91
70°	37.80	62.97	3.19	1.38	49.70	48.78	50.39
77.5°	34.44	58.95	3.27	1.22	46.09	45.06	46.70

(a) Subscript 1 refers to nitrogen
2 refers to oxygen

APPENDIX

Vapor Pressure of Nitrogen

George T. Armstrong

Journal of Research of the National Bureau of Standards Vol. 53, No. 4, October 1954 Research Paper 2543

Vapor Pressure of Nitrogen [1]

George T. Armstrong

The vapor pressure of nitrogen has been measured in the liquid range below the normal boiling point and can be represented by log P (mm) $=6.49594-255.821/(T-6.600)$. The normal boiling point calculated from this equation is 77.364° K. Nitrogen vapor densities along the saturation line are represented by log $\rho T=3.39858-282.953/(T-3.83)$. The fugacity function ln f/p for the saturated vapor is tabulated.

1. Introduction

In the course of a study of the vapor-liquid phase behavior of mixtures of oxygen and nitrogen a series of measurements has been made on the vapor pressure of pure liquid nitrogen. These measurements cover the liquid range below the normal boiling point.

2. Description of Cryostat

The cryostat was designed for liquid-vapor equilibrium studies of mixtures and thus contains several features not essential to the vapor-pressure studies. The following description of the apparatus covers only those portions of the apparatus essential to the measurements.

The equilibrium vessel, in which the liquid nitrogen was contained is a cylinder having walls of ⅛-in. copper and an inner diameter of 1 in. The thermometer is in a well suspended from the upper lid. In these experiments the quantity of liquid nitrogen was insufficient to touch the thermometer well, so that reliance was placed on the uniform-temperature environment and the high thermal conductivity of the copper walls of the equilibrium vessel to insure that the thermometer and liquid were at the same temperature. The equilibrium vessel is suspended by thin-walled tubes within a copper can, which may be evacuated or filled with helium gas for heat transfer. This can forms a constant-temperature enclosure for the equilibrium vessel. It is completely immersed in a constant-temperature nitrogen bath. The temperature of this bath is maintained at the desired operating temperature by regulating the pressure under which it boils with the aid of a cartesian-diver manostat.

To reduce losses of liquid nitrogen from the constant-temperature nitrogen bath, and thus permit longer operation before refilling is required, the constant-temperature bath is immersed in a secondary liquid-nitrogen bath, which is allowed to boil freely at the prevailing atmospheric pressure.

The manometer tube passes through each of the liquid baths. The thermometer leads are brought through a tube into the helium-filled space surrounding the equilibrium vessel. To insure that they are at the bath temperature the leads are wound several times around the pumping tube, which projects into the helium-filled space, and are cemented to the tube.

[1] This research was supported by the Air Research and Development Command, Department of the Air Force.

3. Temperature Measurement

Temperatures were measured with a capsule-type platinum resistance thermometer immersed in a well in the lid of the equilibrium vessel. This thermometer was calibrated against the National Bureau of Standards provisional temperature scale below the the oxygen point [1] [2] and was checked at the oxygen point during the course of the measurements.

4. Pressure Measurement

The manometer used is a version of one described by Swindells, Coe, and Godfrey [2] modified in such a way as to make an absolute pressure-reading instrument. In this manometer the mercury surfaces are located by touching them with stainless-steel rods of calibrated lengths. The contacts are detected electrically, in this instance, by observing the extinction of a lighted neon bulb when a contact is made. The manometer has one fixed contact in the arm connected to the vapor-pressure apparatus. The other arm is closed and evacuated. The detecting rods are introduced into the closed arm through a mounting that can be moved vertically to bring the rod into contact with the mercury. After a contact is made, the position of the upper end of the movable rod is determined with the aid of a micrometer depth gage reading in millimeters. The manometer reads directly to 0.01 mm, and it is possible to interpolate to about 0.002 mm. The manometer as used in these measurements did not provide readings of this accuracy, because the temperature control of the mercury column was not sufficiently good. Errors as large as 0.015 mm or perhaps somewhat larger may have been introduced at times because of uncertainty in the mean temperature of the mercury column.

The measuring rods were calibrated by the Gage Section of the National Bureau of Standards. Thirty-seven quarter-inch stainless steel rods differing in length by increments of 1 in. permitted complete coverage of the pressure range. The rods have a conical lower end with a rounded tip of approximately 1/32-in. radius. The upper end of each is capped by a ¾-in. sphere of bearing bronze, against which the micrometer contact is made. The under surface of the sphere forms a vacuum tight but easily demountable seal against a conical opening through the movable mounting at the top of the closed arm of the manometer.

[2] Figures in brackets indicate the literature references at the end of this paper.

Mercury heights determined in this manometer were corrected to 0° C for thermal expansion of the rods and of mercury, and to a standard gravity of 980.665 cm sec^{-2}. The tube bore is 1 in., and so the necessity for capillary corrections was eliminated. This diameter also insures that the mercury surface is flat enough that the centering of the longer rods does not have to be closer than about 2 mm.

A small correction to the pressure was applied to compensate for the pressure difference between the mercury surface and the liquid-nitrogen surface caused by the greater density of the cold gas in the cryostat. This correction at most amounted to 0.08 mm and was very nearly proportional to the pressure in the system.

5. Material Investigated

The nitrogen used in the experiments was Linde Air Products Company standard high-purity dry nitrogen. This was stated by the supplier to contain less than 0.005 percent of argon. A calorimetric study of the melting point of a similar sample as a function of the fraction melted indicated that liquid-soluble solid-insoluble impurities amounted to much less than 0.01 percent. The material used in the last series of vapor-pressure measurements was analyzed by mass spectrometer after the measurements had been completed and was found to contain approximately 0.01 percent of oxygen. This sample had been in the vapor-pressure apparatus for approximately 2 weeks under reduced pressure, so it is probable that the oxygen entered from the walls or by seepage through stopcock grease, and it may have entered after the measurements were completed. In any case, the maximum effect produced by this amount of oxygen would be 0.06 mm at 760-mm total pressure.

6. Experimental Procedure and Results

In order to insure purity of the nitrogen introduced into the system, the connecting lines to the high-pressure cylinder were evacuated and filled several times and left full of nitrogen at a pressure slightly greater than atmospheric. The remainder of the apparatus was then evacuated overnight at a pressure below 10^{-4} mm. It was then filled with nitrogen, and the cryostat was cooled. Approximately 2 liters of gas was then condensed into the sample holder. The amount condensed was varied in some of the early measurements, and no effect on the measured pressures was observed. After filling the apparatus, all parts except the manometer were closed off by means of stopcocks.

It was impossible to keep the temperature absolutely steady. Drifts observed were of the order of 0.01 deg in 5 min at the lower temperatures and one-half to one-third this rate near the normal boiling point. A series of alternate temperature and pressure measurements was made over a period of 10 min to ½ hr. These were plotted as a function of time, and for each pressure reading a corresponding temperature was found by interpolation. Each value thus determined has been treated as a separate point, though in a sense the measurements of a series are not independent.

Because there was no stirring in the nitrogen constant-temperature bath, a period of 1 or 2 hr was needed to fix the temperature of the bath at a new value and to allow equilibrium to be reestablished. It was thought to be advantageous to start the measurements at a low temperature and to allow the temperature to rise between measurements. This procedure insured that the sample vessel, which always lagged the bath in temperature, would never be at a higher temperature than any part of the bath through which the manometer tube passed.

The measurements made on several different days, and using several different fillings of nitrogen, showed no consistent differences from one another. All measurements made in runs 1, 2, and 3 are shown in table 1. The only measurements not shown are some earlier ones in which the bath level was not properly controlled and in which the manostat regulating the bath pressure was not functioning properly. They showed large and erratic fluctuations, which did not appear again when these two factors were corrected.

TABLE 1. *Vapor pressure of liquid nitrogen*

Log P (mm)	T° K (observed)	$\Delta T\times10^3$ (observed minus calculated)
Series 1		
2.89075	77.5578	−1.1
2.89040	77.5535	+1.5
2.89037	77.5521	+0.7
2.89025	77.5495	+.4
2.89119	77.5693	+1.7
2.89111	77.5665	+0.5
2.89114	77.5678	+1.2
2.89188	77.5820	+0.9
Series 2		
2.83444	76.4686	+1.0
2.83450	76.4697	+0.9
2.83453	76.4704	+1.1
2.79033	75.6344	−1.6
2.78979	75.6267	+0.8
2.78929	75.6181	+1.5
2.78910	75.6130	−0.0
2.78944	75.6186	−.8
2.56364	71.6574	+.8
2.56370	71.6580	+.8
2.35740	68.4412	[a]+27.0
2.35715	68.4386	[a]+28.2
2.35713	68.4370	[a]+26.9
2.27544	67.2135	+0.6
2.27547	67.2137	−.8
2.27556	67.2137	−2.3
2.21875	66.4091	−0.5
2.21881	66.4102	−1.7
2.21894	66.4121	−2.5
2.11814	65.0373	+1.5
2.11837	65.0390	+0.1
2.11864	65.0419	−.6
2.05277	64.1776	+1.5
2.05289	64.1777	0.0
2.05296	64.1778	−.8
Series 3		
2.89479	77.6398	+1.4
2.89486	77.6406	+0.8
2.89487	77.6412	+1.2
2.89594	77.6607	−0.4
2.89611	77.6654	+.9
2.11060	64.9360	+0.7
2.11127	64.9452	+1.0
2.11159	64.9495	+1.0
2.21273	66.3274	+1.1
2.21284	66.3291	+1.2
2.24894	66.8354	−0.2
2.24995	66.8501	+.2
2.25058	66.8576	−1.2
2.89618	77.6638	−2.1
2.89619	77.6642	−1.9
2.89618	77.6644	−1.5
2.21036	66.2920	−1.3
2.21138	66.3088	+1.3
2.21457	66.3500	−2.0
2.27468	67.1998	−3.1
2.27418	67.1959	+0.2
2.27402	67.1915	−1.9
2.35593	68.3915	−0.7
2.35591	68.3916	−.3
2.35609	68.3939	−.7
2.42898	69.5017	−.4
2.42905	69.5036	+.4
2.42917	69.5054	+.3
2.50438	70.6901	−.2
2.50457	70.6933	−.1
2.50473	70.6966	+.7
2.58980	72.0941	+2.2
2.58991	72.0952	+1.5
2.59002	72.0968	+1.3
2.69836	73.9597	−1.3
2.69871	73.9709	+0.7
2.69917	73.9797	+1.3
2.85437	76.8532	+3.2
2.85470	76.8594	+3.0
2.85472	76.8593	+2.5
2.85465	76.8579	+2.5

[a] Discarded by Chauvenet's criterion.

The data have been fitted by the Antoine-type equation (1)

$$\log P(\text{mm}) = 6.49594 - 255.821/(T - 6.600). \quad (1)$$

Aside from three points at 68.4°, the measurements lie within a narrow band about eq (1). For these three points the observed and calculated pressures differ by very nearly 1 mm, so it is possible that an error was made in reading the micrometer depth gage. These three points were discarded on the basis of Chauvenet's criterion. The mean deviation from eq (1) of all measurements except those specified above is ±0.0012 deg K, or ±0.063 mm. It is possible that a slightly better fit could be obtained by the use of an additional constant or a different functional form of an equation because there appears to be a slight cyclic trend of the deviations. An estimation of the best fit in the form of a smooth curve drawn through the deviations suggests that the mean deviation could not be reduced below 0.0010 deg K by any other simple equation.

The normal boiling point calculated from eq (1) is 77.364 deg K. Some other experimental values are shown in table 2 [3 to 8]. The standard deviation in this temperature, which was found to be ±0.0013 deg for the present work, indicates only the internal precision of the data and does not give any indication of the reliability of the temperature scale. The values obtained by Henning and Otto [6] and by Keesom and Bijl [7] are very close to the present value. The value of 77.34 deg reported by Friedman and White [8] is obtained from their equation. Their value is subject to an uncertainty of 0.05 to 0.07 deg because of the deviation of their equation from their experimental values in the immediate vicinity of the boiling point.

A comparison of the experimental data from several laboratories with eq (1) is shown in figure 1. The deviations shown in table 1 have been omitted from figure 1 in order to avoid a confusion of points near the reference line. The present data are in good agreement with the data of Keesom and Bijl, showing only small systematic deviations. The rather large deviations of the data of Henning and Otto are not easy to account for because they are erratic; on the other hand, the deviations of the data of Giauque and Clayton are very systematic. The systematic deviations in the work from various laboratories are probably due to differences in the temperature scales. It is unlikely that any further improvement in the consistency of the vapor-pressure data of nitrogen will be made until the temperature scales used in various laboratories are brought into agreement in this region.

Table 2. *Normal boiling point of nitrogen*

Investigators	Date	T_B
		°K
Dodge and Davis [3]	1927	77.36
Heuse and Otto [4]	1932	77.346
Giauque and Clayton [5]	1933	77.32
Henning and Otto [6]	1936	77.352
Keesom and Bijl [7]	1937	77.373
Friedman and White [8]	1950	77.34
This research	1954	77.364

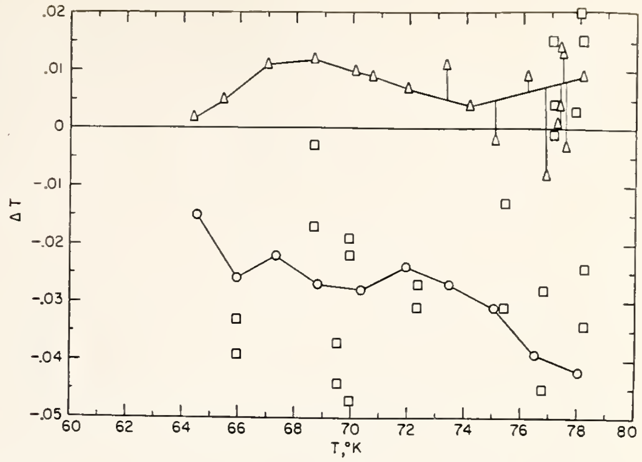

Figure 1. *Deviations (observed minus calculated) of other experimental values from equation 1.*

△, Keesom and Bijl; ○, Giauque and Clayton; □, Henning and Otto.

7. Calculation of Saturated Vapor Volume and Fugacity

Vapor-pressure data have at times been used for calculating the latent heat of vaporization, using the formula $\Delta H = T(V_g - V_l)dP/dT$. The vapor volume of nitrogen is, however, probably not as well known as the other quantities required in this formula. The only direct experimental measurements of this quantity were those of Mathias, Onnes, and Crommelin [9]. These were revised by Crommelin for inclusion in the International Critical Tables [10], using a reduced equation of state, but it is questionable whether any improvement resulted.

Because the heat of vaporization has been accurately measured by Furukawa and McCoskey [11], their data have been combined with the present vapor-pressure data to calculate the saturated vapor density at several temperatures. The liquid volumes used were those of Mathias, Onnes, and Crommelin. The saturated vapor density derived from the vapor-pressure data may be represented by eq (2), where ρ is the vapor density in grams per cubic centimeter,

$$\log \rho T = 3.39858 - 282.953/(T - 3.83). \qquad (2)$$

Table 3. *Saturated vapor density of nitrogen*

T	ΔH(vapor)[11]	$\rho \times 10^3$ (g/cm³)			
		1	2	3	4
°K	*abs j mole⁻¹*				
64.80	------------	0.883	------	0.89	0.868
67.71	------------	1.376	------	1.36	------
68.00	6775.0	1.434	1.434	------	------
73.10	5735.2	2.818	2.818	------	------
73.13	------------	2.828	------	2.78	------
77.364	5593.0	4.593	4.593	------	------
78.00	5571.8	4.915	4.916	------	------
78.07	------------	4.952	------	4.90	4.98

TABLE 4. *Fugacity function of nitrogen*

T	$\ln f/p$
°K	
64	−0.0096
66	−.0127
68	−.0163
70	−.0205
72	−.0250
74	−.0297
76	−.0348
78	−.0409

In column 1 of table 3 are shown values of vapor density calculated from eq (2). The values from which this equation was derived are shown in column 2; those given by Mathias, Onnes, and Crommelin are listed in column 3, and the revised values presented by Crommelin are shown in column 4.

The densities calculated from the vapor-pressure data are seen to be intermediate between the observed and revised values of Mathias, Onnes, and Crommelin. It should be noted that the revised value for the vapor density given by Crommelin at 64.80° K is incompatible with the behavior of a real gas near its saturation line, as it is less than ideal gas density at this temperature and pressure.

Using eq (2) for calculating vapor volumes, the fugacity of nitrogen along the saturation line has been calculated and is shown in the form $\ln f/p$ in table 4. There are no experimental data for this quantity derived from PVT measurements below 80°. However, extrapolations of higher-temperature data from various sources give values that are in some cases larger and in other cases smaller than those listed in table 4.

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WASHINGTON, May 18, 1954.

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Functions and Activities

The functions of the National Bureau of Standards are set forth in the Act of Congress, March 3, 1901, as amended by Congress in Public Law 619, 1950. These include the development and maintenance of the national standards of measurement and the provision of means and methods for making measurements consistent with these standards; the determination of physical constants and properties of materials; the development of methods and instruments for testing materials, devices, and structures; advisory services to Government Agencies on scientific and technical problems; invention and development of devices to serve special needs of the Government; and the development of standard practices, codes, and specifications. The work includes basic and applied research, development, engineering, instrumentation, testing, evaluation, calibration services, and various consultation and information services. A major portion of the Bureau's work is performed for other Government Agencies, particularly the Department of Defense and the Atomic Energy Commission. The scope of activities is suggested by the listing of divisions and sections on the inside of the front cover.

Reports and Publications

The results of the Bureau's work take the form of either actual equipment and devices or published papers and reports. Reports are issued to the sponsoring agency of a particular project or program. Published papers appear either in the Bureau's own series of publications or in the journals of professional and scientific societies. The Bureau itself publishes three monthly periodicals, available from the Government Printing Office: The Journal of Research, which presents complete papers reporting technical investigations; the Technical News Bulletin, which presents summary and preliminary reports on work in progress; and Basic Radio Propagation Predictions, which provides data for determining the best frequencies to use for radio communications throughout the world. There are also five series of nonperiodical publications: The Applied Mathematics Series, Circulars, Handbooks, Building Materials and Structures Reports, and Miscellaneous Publications.

Information on the Bureau's publications can be found in NBS Circular 460, Publications of the National Bureau of Standards ($1.25) and its Supplement ($0.75), available from the Superintendent of Documents, Government Printing Office. Inquiries regarding the Bureau's reports and publications should be addressed to the Office of Scientific Publications, National Bureau of Standards, Washington 25, D. C.

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