[CONTRIBUTION FROM THE CRYOGENIC ENGINEERING LABORATORY OF HARVARD UNIVERSITY]

AN INVESTIGATION OF THE COEXISTING LIQUID AND VAPOR PHASES OF SOLUTIONS OF OXYGEN AND NITROGEN[1]

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Introduction

The properties of the coexisting liquid and vapor phases of the system: oxygen–nitrogen, constitute the fundamental data of the air-separation industry. One of the objects of this investigation was to obtain these data over a much wider range of pressure and temperature than had hitherto been covered. While such data may not be of great use in the present methods of air separation, the object of which is the production of compressed oxygen for the welding and cutting of metals, or of nitrogen for the synthesis of ammonia, yet it is believed that such data will be of considerable service in the future development of the art of air separation. It is believed by those who have given the subject serious consideration, that further development will eventually lead to the production of oxygen on so large a scale and at so low a cost that many high-temperature operations such as the smelting of metals, manufacture of producer gas, and the like, will utilize oxygen or air enriched with oxygen in preference to ordinary air, with resulting economies.

In addition to their industrial significance the data herein presented are a contribution to the theory of binary solutions. A large amount of work has been done on binary solutions of completely miscible liquids but most of it has been confined to a study of the systems at or near atmospheric pressure. Very few systems have been studied over a range of pressure and temperature. In this investigation the system: oxygen-nitrogen has been studied from pressures below one atmosphere up to nearly the critical pressure of nitrogen or from a temperature of 77–125°K. Of the five variables which completely define the state of such a system only four have been considered in this work, namely, the pressure and temperature and the composition of each phase.

The first scientific investigation of this system was that of Baly,[1a] who measured the temperature and the compositions of both phases at a constant pressure of one atmosphere. He found the two components to be miscible in all proportions and to give the simple type of *t-x* diagram without a maximum or minimum boiling point. Baly's temperature meas-

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[1] Abstracted from a thesis presented in 1925 to the Faculty of the Harvard Engineering School by Barnett F. Dodge for the degree of Doctor of Science. The experimental work was begun by A. K. Dunbar, who was killed in 1922 by the explosion of an oxygen cylinder, and completed in 1925 by the other author.

[1a] Baly, *Phil. Mag.*, [V] 49, 517 (1900).

urements are now known to be considerably in error and the results of the present investigation also show that his values for the phase compositions are also only approximate.

The only other investigation of this system was that of Inglis,[2] who measured the pressure and the composition of both phases along two isothermals, namely, $T = 74.7$°K. and $T = 79.07$°K. As will appear later, Inglis' results fit in very well with our own for higher temperatures. Other investigations of binary systems of this type at low temperatures are those of Inglis[2] on the system: oxygen-argon at 82.1°K. (only a few points obtained), of Holst and Hamburger[3] on argon-nitrogen at various temperatures and pressures in the immediate neighborhood of 90°K. and of Dunbar and Davis[4] on mixtures of methane and nitrogen, and of oxygen and nitrogen.

Discussion of Methods Investigated for the Establishment of Phase Equilibrium

A vast amount of work has been done on the investigation of the phase relations of completely miscible liquids at ordinary temperatures, and the same methods of securing equilibrium may be used at low temperatures. In the course of this work a general survey of possible methods was undertaken, and several were tried before selecting the one finally used. The simple dynamic or distillation method, in which a small amount of the vapor phase is distilled from a relatively large amount of liquid without any stirring and collected as the average equilibrium vapor phase, was tried in comparison with other methods. This was the method used by Baly,[1a] and it has been extensively used in work on mixtures of organic liquids at room temperatures, notably by Zawidzki[5] and Lehfeldt.[6]

With our particular apparatus we found this method to give a 1–2% smaller spread between the liquid and vapor compositions than two other methods to be described. This is undoubtedly due to the fact that the liquid does not remain homogeneous, the upper layers becoming enriched with the less volatile component in spite of the fact that the rate of distillation was such as to remove only 0.1% of the total liquid phase per minute. Other investigators have improved this method by the use of a mechanical stirring device, but such a device would have been very difficult to apply in this case.

The method devised by Rosanoff, Lamb and Breithut[7] was adapted by

[2] Inglis, *Phil. Mag.*, [VI] 11, 640 (1906).

[3] Holst and Hamburger, *Z. physik. Chem.*, 91, 513 (1916).

[4] Dunbar and Davis, unpublished work done at the Cryogenic Laboratory of Harvard University.

[5] Zawidzki, *Z. physik. Chem.*, 35, 129 (1900).

[6] Lehfeldt, *Phil. Mag.*, [V] 46, 42 (1898).

[7] Rosanoff, Lamb and Breithut, THIS JOURNAL, 31, 448 (1909).

Dunbar and Davis[4] for use at low temperatures. This method consists in passing a vapor mixture of constant composition through a liquid mixture of approximately the proper composition for phase equilibrium with the vapor. The liquid will adjust itself to the equilibrium composition and this is indicated by constancy of successive vapor samples. When this steady state is reached, any desired amount of vapor may be collected for analysis. The steady flow of vapor through the liquid also acts as an efficient stirrer. The main difficulty with this method at low temperatures lies in the production of the steady flow of vapor of constant composition, which at room temperatures is obtained simply by boiling a liquid mixture and adding the more volatile component at such a rate as to keep the boiling point constant. For low-temperature work this was accomplished by storing the vapor as a gas mixture in a cylinder under pressure at room temperature. Before reaching the liquid it was cooled by interchange with outgoing cold vapor and finally by passing through the low-temperature bath. Very careful regulation of the gas flow was necessary and this was accomplished by means of a plunger valve (See Fig. 2). Good results were obtained with this method but it was abandoned mainly for the following reasons. (1) No satisfactory method was available for gaging the inflow of gas under the widely varying pressures encountered. Variation in liquid level was used to gage this flow but was entirely too insensitive. (2) The necessity for preparing in advance of a run, a gas mixture of the approximately correct composition for phase equilibrium with the given liquid phase and storing this under a pressure considerably greater than the equilibrium vapor pressure, made the method a tedious and time-consuming one in a case where pure gases were to be used.

The method finally adopted was a modification of that used by Inglis[2] which consisted in recirculating the vapor distilled from the liquid, by means of a mercury pump, back through the liquid by way of a heat-interchange system. In this way the liquid was stirred and equilibrium insured by continually bringing the vapor into contact with the liquid.

Description of Apparatus and Methods of Measurement

Cryostat and Recirculation Pump.—The cryostat or low-temperature bath for the maintenance of constant temperatures and the equilibrium chamber containing the system under investigation are shown in Fig. 1.

The cylindrical container C of about 2 liters' capacity is spun from a 3in. (7.6cm.) copper tube. It is closed at the bottom by squeezing the copper between the two threaded brass pieces A and B and "sweating" soft solder into the joints. A flange is spun at the top of C to which the brass flange E is soldered. The brass cover D is bolted to the flange E, using a lead gasket F to obtain a gas-tight joint. Copper tubes T, X and Y, soft-soldered into the cover D, serve, respectively, for introducing the bath liquid, removing the gas and measuring the pressure. The equilibrium chamber holding the mixture under investigation consists of a brass tube G closed at the top by the plug H and into the bottom of which is screwed the copper piece I, hollowed out as shown and on the outer surface of which is cut a triple screw thread. Gas enters the equilibrium chamber through L, which branches at J into 3 small tubes, each one of which opens into one of the depressions between the screw threads. The gas is thus forced to take a helical path through the liquid, increasing the time of contact and at the same time conveying some liquid by an "air-lift" action. Small holes are drilled from the trough of each thread to the hollow central portion of I so that the liquid in the vessel is presumably stirred by the "air-lift" action. Q is the gas exit tube, protected from direct contact with the oxygen bath by the jacket R. Tube K serves to contain the two-couple copper-constantan thermo-element used for temperature measurement. The small copper tube M served to locate the liquid level in some of the preliminary measurements and later to withdraw samples of the liquid phase. This tube is attached at its upper end to a valve which can be moved up and down through a stuffing box (e in Fig. 3), so that the position of Tube M in the equilibrium chamber can be varied. The lower end of the heat interchanger between inlet and exit gas is shown at UV. The whole cryostat is surrounded with about 7.6 cm. of mineral wool for thermal insulation.

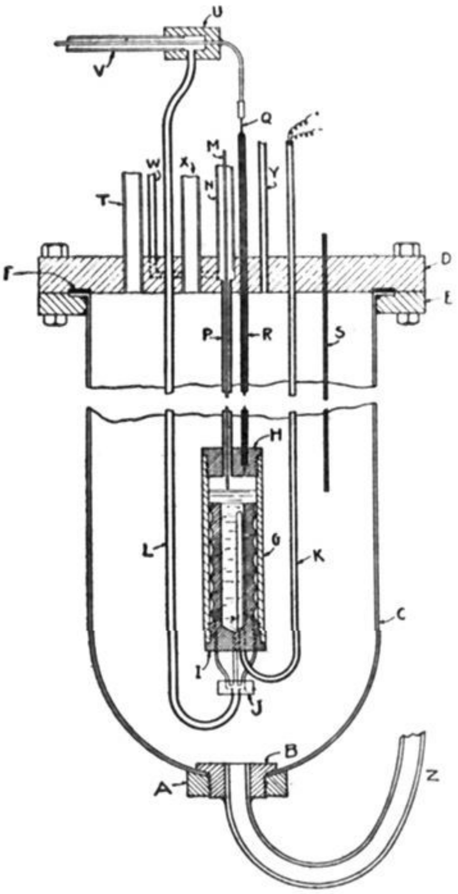

Fig. 1.—Details of the cryostat.

For temperature control, the cryostat vessel C was filled through Tube T with liquid oxygen. By maintaining a constant pressure on the boiling oxygen in the range from 130 mm. absolute to 300 lbs. per sq. in. (20 atm.), constant temperatures ranging from 76.5° to 135°K. were obtained. Pressures below 1 atmosphere were obtained by means of a two-stage Packard vacuum pump of 5.5 cu. ft. (155.7 liters) per min. displacement. Pressures above 1 atmosphere were controlled by means of a standard relief valve for the coarse adjustment and a plunger valve of the type shown in Fig. 2 for the fine adjustment.[8] Regulation of flow with this valve is obtained by varying the length of the annular space between the plunger H and the cylinder L. This type of valve was found to be exceedingly useful for very fine adjustment of flow.

As an indication of the constancy of the pressure control we at first used the variation of the pressure or the temperature of the system under investigation, but because of the time lag this was not as sensitive as desired. Consequently, a better method was devised which gave an immediate indication of the effect of the valve adjustment on the pressure of the boiling oxygen. The general principle of the scheme consists in communicating the pressure that is to be maintained in the cryostat to a

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[8] The essential features of this valve are due to Professor F. G. Keyes of the Massachusetts Institute of Technology.

constant-volume system, keeping this pressure constant by holding the temperature constant, and then continually adjusting the cryostat pressure to equality with this "artificial atmosphere" through a differential manometer. Referring to Fig. 3, which is a diagram of the whole cryostat set-up, B is the bomb, constructed of extra strong pipe fittings, that holds the artificial atmosphere, maintained at constant temperature by the thermostat A. The cryostat pressure is adjusted to the approximate value desired by the relief valve D, then this pressure is communicated to B by opening Valve 1 (Valves 2, 3, 4 and 5 being closed). The differential manometer F may then be brought into action by cautiously opening Valves 2 and 3 so as to place the cryostat pressure on both sides of the liquid. (Manometer F, filled with mercury, was used for pressures above 2 atmospheres and G, filled with kerosene, was used for all pressures up to 2 atmospheres.) The manometer tubes are of heavy glass and are sealed to the copper pressure leads by means of brass pieces, into one end of which the copper tube is soldered and into the other end of which the glass tube is loosely fitted and sealed with shellac cement.

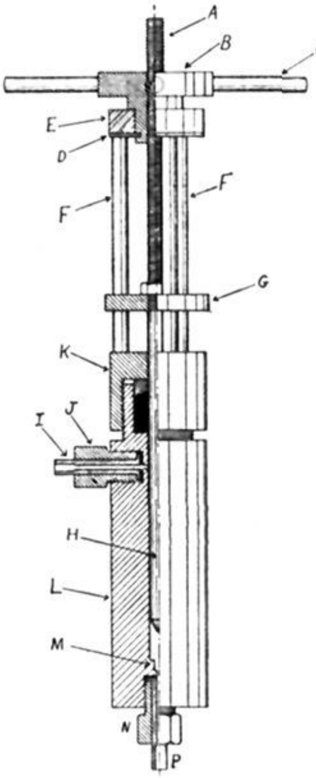

Fig. 2.—Plunger valve for the regulation of gas flow.

The cryostat pressure is adjusted to the exact value desired (as indicated by the temperature) by means of the plunger valve H (see Fig. 2 for details) and then the by-pass is closed by closing Valve 1. Since the pressure in B remains constant after Valve 1 is closed, variations in pressure in the

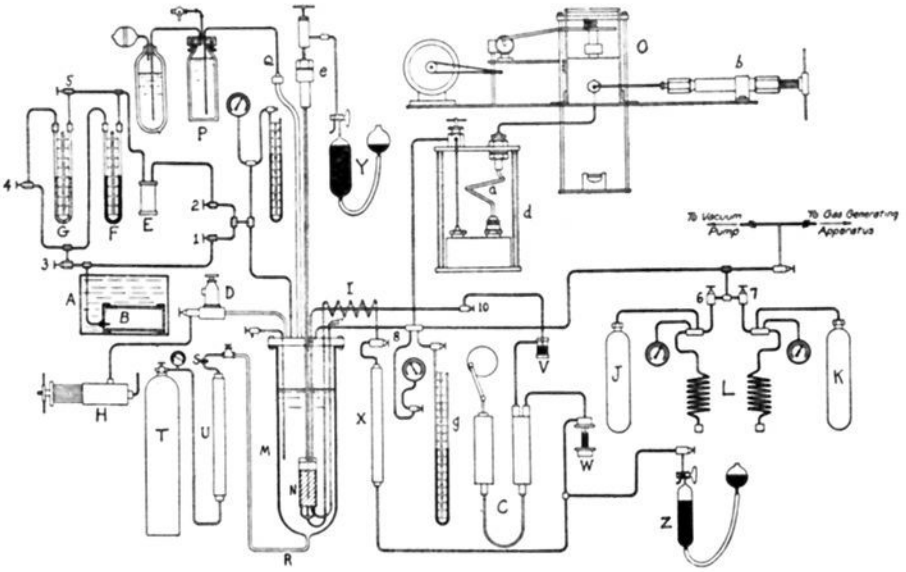

Fig. 3.—Diagrammatic sketch of the apparatus.

cryostat will be sensitively indicated on F (or G) and by regulating the plunger valve H so as to keep the level constant in the manometer, the temperature may be controlled to 0.01–0.02°. The temperature of A need not be controlled to better than 0.05°, and the effect of temperature variation along the connecting tubing can be made negligible by a suitable choice of the volume of B in relation to the volume of the tubing.

The recirculation of the vapor was accomplished by a mercury-column pump indicated at C in Fig 3. This pump consists of two cylinders of cold-rolled steel with a 6mm. hole drilled in each, connected together to make a U by means of steel tubing and flared tubing unions. The mercury is made to oscillate by a steel piston working in one of the cylinders, driven by a motor, direct-connected through a train of gears to a crank and a cross-head. The flow of gas in and out of the pumping cylinder is controlled by two mercury valves.

The development of the recirculation system was due to Victor Yngve, who was formerly a Fellow in Cryogenic Engineering at Harvard University. The pump was originally provided with mechanical valves, but these were not satisfactory. Yngve added a mercury outlet valve which also served as a sight glass to allow the operator to observe whether or not the pump was functioning properly. Later, we added a mercury inlet valve which further improved the operation of the pump.

Temperature Measurements.—These were made with a thermo-element consisting of two copper-constantan thermocouples in series inserted in a closed copper tube for protection from the oxygen bath. The tube was well immersed in the liquid phase of the system under investigation as shown at K in Fig. 1. The e.m.f. was measured with a slide-wire type of potentiometer. The electrical set-up was made in accordance with the directions of White,[9] including the circuit for the elimination of parasitic e.m.f.'s. The potentiometer could be read to about 0.5 microvolt and this e.m.f. was equivalent to about 0.015°C. at 90°K. The potentiometer was calibrated every one-tenth of a turn on the slide wire by balancing against known e.m.f.'s obtained from a circuit containing a storage battery and a set of standard resistances, the current in this circuit being frequently checked up by means of a standard cell.

The thermocouple was calibrated by measuring its e.m.f. at three fixed points. The fixed points used were the normal boiling points of nitrogen, oxygen and methane, for which the following values were chosen: nitrogen, normal b. p.[10] = —195.80°C., or 77.33°K.; oxygen, normal b. p.[10] = —182.97°C., or 90.16°K.; methane, normal b. p.[11] = —161.61°C., or

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[9] White, This Journal, **36**, 1856 (1914).

[10] (a) Cath, *Comm. Phys. Lab. Leiden*, No. 152d. (b) Henning and Heuse, *Z. Physik*, **23**, 105 (1924).

[11] Keyes, Taylor and Smith, *J. Math. Phys. Mass. Inst. Tech.*, **1**, 211 (1922).

111.52°K. Values in °C. are on the centigrade thermodynamic scale and values on the Kelvin scale are obtained on the assumption of 273.13°K. for the ice point. For each substance a series of pressure and e.m.f. measurements was made in the neighborhood of the normal boiling point and the e.m.f. for $p = 1.000$ atmosphere was obtained from a plot. For interpolation and extrapolation an equation of the type used by Adams[12] was applied to our e.m.f.-temperature data at the three fixed points. The deviations between the e.m.f. as given by this equation and the e.m.f. of Adams' standard couple were then plotted against the e.m.f. of Adams' couple. This deviation plot combined with the interpolation table published by Adams furnished a convenient and accurate method of obtaining the temperature from the potentiometer observations. Adams' table gives the temperature for every hundred microvolts and to increase the accuracy we found it advisable to extend the table to one giving the temperature for every five microvolts.

From the results of vapor-pressure measurements on nitrogen, oxygen and methane to be given in a separate paper, it is believed that the temperature scale established by the above method is accurate to approximately 0.1°C. over the range covered.

Pressure Measurements.—Bourdon gages were used for approximate pressure measurements purely as an aid to control of the operation. Pressures up to 5 atmospheres were read on a mercury column (g in Fig. 3) provided with a graduated steel tape for a scale, the barometric reading being obtained at the same time. The usual corrections for temperature were made. Since the rate of change of vapor pressure at these low temperatures is great, pressure measurements to 0.5 mm. are well within the pressure variation caused by fluctuation of the temperature even at the lowest pressures. Above 5 atmospheres, pressures were determined by a dead-weight piston gage constructed at the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology. This gage is shown at O in Fig. 3; b is an oil injector to make up for the leakage of oil around the piston, and d is an indicator to show when the piston is in equilibirum, the indication being given by the motion of an oil-mercury meniscus in the glass capillary a. The constant of this gage (0.99856 mm. of mercury per g.) was determined by comparison with a mercury column reading to about 12 atmospheres. The average deviation from the mean of seven determinations of the constant was 0.008%.

Sampling and Analysis of Liquid and Vapor Phases.—No difficulty at all was experienced in obtaining a true sample of the vapor phase but considerable work was necessary before a satisfactory liquid-phase sampling method was devised. Inglis[2] experienced considerable difficulty in obtaining concordant liquid samples and finally obtained samples that agreed

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[12] Adams, *Bull. Am. Inst. Min. Met. Eng.*, No. 153, 1919.

to 0.3% by the use of fine capillaries for sampling tubes. Dunbar and Davis[4] made extensive experiments with capillary tubes and tubes with ball check valves in an attempt to develop a method that would give reproducible results at low rates of flow (20 cc. of gas per min., measured at 1 atm. and room temperature), without success. They finally resorted to total evaporation of the liquid phase to a storage reservoir with subsequent withdrawal of a small gas sample. This method is out of the question if consecutive runs are to be made on a given liquid phase, and at high pressures the very uncertain corrections due to dead space and inclusion of some of the vapor phase in the sample become large. The method finally adopted in this investigation consisted in the use of a fine copper capillary about 0.2 mm. internal diameter and 25.4 cm. long, connected to a larger tube and a valve, the sample being withdrawn at a rate of not less than 100–200 cc. per minute (measured as gas after expansion). A large number of tests showed that consecutive samples checked to 0.2% in the worst case and usually to better than 0.1%. All samples were collected over mercury, previous tests having shown that samples taken over water or salt solutions could not be relied on to better than 0.5% unless analyzed at once.

All analyses were made by the usual method of absorption at constant pressure, using a compensated mercury buret. The leveling bulb of the buret rested on a carriage which could be moved up and down by a fine screw and the pressure adjustment was indicated by a mercury manometer with an electric-contact device, so that a given reading of the buret could be reproduced to 0.01 or 0.02 cc. For absorbent, the potassium pyrogallate solution as recommended by Benedict[13] was used and found very satisfactory. With this apparatus check analyses within 0.05% of oxygen were regularly made. The absolute accuracy of the analyses may be judged from the fact that a series of determinations of the oxygen content of ordinary air gave an average of 20.93% of oxygen, which is in close agreement with the best accepted value.

Preparation and Storage of Gases.—Nitrogen was prepared by dropping sodium nitrite solution into a solution of ammonium sulfate maintained at about 95°C. The gas was passed in succession through concd. sulfuric acid, solid potassium hydroxide and phosphorus pentoxide and finally freed from oxides of nitrogen by repeated distillation. To condense the gas, the condensation bulb was surrounded with liquid nitrogen from an air-separation column through which hydrogen was bubbled to lower the temperature. The apparatus was similar to that used by Smith and Taylor,[14] and hence need not be described in detail. Considerable nitric oxide was always present in the crude nitrogen, but a few distillations served to remove all but the last traces (less than 0.01%).

Oxygen was obtained through the kindness of Dr. H. W. Starkweather of Harvard

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[13] Benedict, *Carnegie Inst. Publ.*, No. 166 (1913).

[14] Smith and Taylor, THIS JOURNAL, **45**, 2107 (1923).

University, from an electrolytic generator and purifying train used by him for the preparation of oxygen for exact determination of its density. The oxygen so prepared was liquefied by cooling with liquid air, transported to the Cryogenic Laboratory as a liquid in a bulb closed by a stopcock and then distilled to the storage system. The preparation of methane for thermocouple calibration was accomplished by the fractionation of natural gas, details of which will appear in a separate paper.

Purified gases were stored in mercury-sealed gasometers and also in small cylinders. Although the use of gasometers was later abandoned in favor of cylinder storage, a brief description of their construction seems warranted as they are believed to be of novel design and may be of considerable use to others. A and B (Fig. 4) are cast-iron drums, machined and fitted together so as to leave an annular space of about 5 mm. for the mercury. The joint at C was made tight with a litharge-glycerol cement. The lugs H, cast on the outer cylinder, were drilled and tapped to take the guide rods F. The floating bell D is a pressed steel kettle of $^1/_{16}$ in. (1.6mm.) stock (a standard blank for an enameled soup kettle). The pieces E for guiding the bell were of angle iron and soldered to the bell. The gas line consisted of a standard $^1/_8$ in. (3.2mm.) pipe nipple, threaded and cemented into the bell and a glass trap L into which was cemented a helix of thin-walled $^7/_{64}$ in. (2.8mm.) copper tubing N to take up the motion of the bell. When the bell is at the top of its travel the mercury level is adjusted to stand about 2.5 cm. below the top of A and as the bell moves down, mercury is displaced into the space above the inner drum B and by the application of a slight suction can be made to fill the space between B and D, thus permitting gas to be completely withdrawn. It was found, however, that the evacuation was not quite complete but probably could be made so by slightly dishing the top of B and of D. Only about 16 kg. of mercury is needed to seal a gasometer of 20 liters' capacity. The castings contained a number of blow holes which were sealed with shellac cement and all surfaces in contact with gas were thoroughly coated with shellac. Tests on such a gasometer showed a slight leakage. For example, pure nitrogen stored under the slight pressure due to the weight of the bell increased in oxygen content from 0 to 0.3% in 64 days. The cause of this increase was not determined, as the gasometers were eventually abandoned in favor of the storage system shown in Fig. 3, mainly because the formation of the liquid phase was greatly facilitated by having the gas under pressure. The pressure storage system consisted of two 2-liter cylinders J and K, each cylinder being connected through a manifold to a pressure gage, valve and liquefying coil. In order to charge a cylinder with gas under pressure, from a gas-generating and purifying train constructed of glass, the cylinder and line are first evacuated, then washed out a few times with the gas to be stored and then the liquefying coil is surrounded with liquid oxygen or nitrogen and the gas from the generating train condensed. When a sufficient amount has been collected, Valve 6 (or

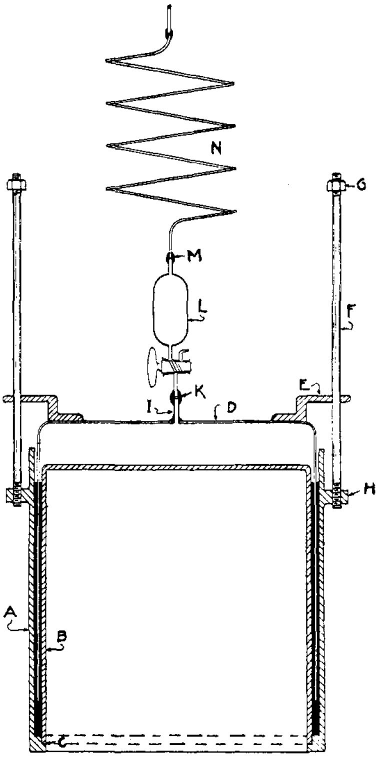

Fig. 4.—Mercury-sealed gasometer.

7) is closed, the refrigerant removed and the liquid evaporates under pressure into the cylinder. Having the gas under considerable pressure greatly facilitates the formation of the liquid phase in the equilibrium chamber N. Knowing the volume of the system, the pressure gage can be used to measure the quantity of gas withdrawn from or added to the system. One cylinder was used for pure oxygen or pure nitrogen and the other for binary mixtures.

Procedure.—The cryostat was first filled with the bath liquid by transferring it from a glass Dewar flask to a metal vacuum bottle (a standard Stanley bottle fitted with a special top shown at P in Fig. 3) and allowing the liquid to force itself in through the line Q by its own vapor pressure. Liquid oxygen from a commercial oxygen column was found to be a very suitable bath liquid. Due to its high purity the temperature change for complete evaporation at constant pressure was not more than 0.02–0.03°C. Liquid nitrogen from the same column was not at all suitable due to its oxygen content, but had to be used at the start of some runs on nitrogen-rich mixtures, when the gases were stored in gasometers and hence no pressure was available for liquefaction. In those cases, it was used only to form the liquid phase and was replaced by oxygen during the actual run. About 5 liters of oxygen must be used to fill the cryostat with 2 liters of liquid. (The bath liquid could be removed at any time from the cryostat by closing all exits, allowing the pressure to build up, then opening the valve in Line R, the union S being broken.) The liquid phase was then formed in the chamber N by placing the appropriate storage cylinder J or K in communication with N. The amount of gas necessary to fill N about three-fourths full was calculated and measured by means of the gages on the storage cylinders.

When the liquid phase was formed, the bath was then brought to the desired temperature. If this temperature is above the normal boiling point of oxygen, upon closing all exits from M the oxygen warms to the desired temperature, but the rate of temperature rise is very slow and a marked temperature gradient develops between the top and bottom of the cryostat. To hasten the rise and keep the temperature uniform, oxygen from a cylinder T, dried by a tower U filled with solid potassium hydroxide, was bubbled through the liquid oxygen. If a temperature below 90°K. was to be maintained, the cryostat was exhausted by the vacuum pump through the line used for introducing the liquid. The control of the pressure to maintain constant temperatures has already been described. Having formed the liquid phase and adjusted the temperature, the valves 8 and 10 were then opened to permit the vapor to enter the previously evacuated recirculation system. The recirculation pump C was then started, which takes vapor from N, through the interchanger I where it cools the returning gas, through the mercury inlet valve V, and forces it through the sight valve W and the reservoir X (whose sole function is to increase the vapor space so that at low pressures a sufficiently large sample may be withdrawn for analysis) back to N where it bubbles through the liquid. During the circulation of the vapor, which was generally at the rate of 40–50 cc. per min., frequent readings of the pressure and temperature were made. Conditions usually became steady about ten minutes after starting the recirculation pump except for the small fluctuations due to variation in the temperature control. The recirculation was continued at least 20 minutes after steady conditions were obtained to make sure of a thorough sweeping of the vapor space. The pump was then stopped, Valves 8 and 10 were closed to isolate the vapor phase from the liquid, and samples of the liquid and vapor phases taken in the mercury-sealed pipets Y and Z, respectively, the sampling lines first being thoroughly swept out. The temperature of the bath may then be changed and another run made on substantially the same liquid phase. To conserve both time and liquid oxygen it was usually found desirable to make four runs on a given liquid phase, one filling of the cryostat bath being good for two runs. At the conclusion of a series of runs, the liquid was evaporated to the storage cylinder by surrounding the liquefying coil with liquid oxygen or nitrogen.

Results of the Investigation

Summary of the Data.—In Table I a summary of the final data is given. Data obtained in a number of runs of a preliminary nature, whose primary object was the development of the method, and in a few runs that were considered doubtful because of too much liquid phase, have not been included.

TABLE I

SUMMARY OF FINAL DATA

Temp., °K.	Press., atm.		Composition (mole % of O_2)		
	Obs.	Corr.	Liquid	Vapor Uncorr.	Vapor Corr.
		I 77°K. Isotherm			
76.79	0.5965	...	49.15	16.62	...
77.36	0.8712	...	15.86	4.59	...
		II 90.5°K. Isotherm			
90.53	1.177	1.174	94.58	82.64	82.63
90.54	1.355	1.360	89.00	69.08	69.06
90.49	1.550	1.551	82.41	56.40	56.40
90.54	1.565	1.559	82.12	55.92	55.89
90.60	1.601	1.586	80.60	53.68	53.63
90.50	1.808	1.808	72.87	43.41	43.41
90.40	2.128	2.145	60.97	31.58	31.63
90.34	2.270	2.302	55.11	27.12	27.20
90.50	2.401	2.401	50.43	24.13	24.13
90.46	2.458	2.467	49.39	23.64	23.64
90.46	2.492	2.501	46.94	21.92	21.94
90.70	2.847	2.799	35.21	15.02	14.96
90.78	3.341	3.262	16.26	6.34	6.30

TABLE I (*Concluded*)

Temp., °K.	Press., atm.		Composition (mole % of O_2)		
				Vapor	
	Obs.	Corr.	Liquid	Uncorr.	Corr.
III 99.94°K. Isotherm					
99.93	2.727	2.729	95.00	86.91	...
99.94	2.903	2.903	92.99	81.35	...
99.93	3.020	3.022	90.05	75.45	...
99.93	3.253	3.256	86.40	68.71	...
100.00	3.468	3.452	82.09	61.06	...
99.92	3.839	3.845	74.88	50.92	...
99.93	4.757	4.760	57.52	33.34	...
99.98	5.058	5.043	51.25	28.71	...
99.93	5.619	5.623	41.03	21.48	...
99.94	5.841	5.841	36.24	18.37	...
99.92	6.631	6.640	19.44	9.23	...
99.93	7.175	7.180	9.14	4.22	...
IV 110.05°K. Isotherm					
110.03	6.025	6.033	93.48	84.83	...
110.11	6.632	6.606	87.34	73.74	...
110.04	7.281	7.286	79.83	62.50	...
110.06	9.237	9.231	58.31	38.56	...
110.03	10.721	10.734	41.92	25.64	...
110.04	11.129	11.136	36.91	22.13	...
110.05	12.651	12.651	20.18	11.61	...
110.05	13.663	13.663	9.55	5.37	...
V 119.92°K. Isotherm					
119.91	11.843	11.850	87.98	78.12	...
119.91	12.873	12.880	80.82	67.63	...
119.95	14.528	14.505	69.10	54.04	...
119.92	15.952	15.952	58.89	43.78	...
119.88	18.029	18.068	44.74	31.54	...
119.88	18.900	18.939	37.51	25.85	...
119.91	21.471	21.482	21.00	14.14	...
119.90	22.958	22.981	11.62	7.89	...
VI 125.00°K. Isotherm					
124.93	15.475	15.531	89.07	79.76	...
124.95	16.814	16.857	80.50	69.05	...
125.06	20.510	20.450	59.63	46.29	...
124.95	22.937	22.992	45.92	...	...
124.98	24.275	24.298	37.75	28.05	...
124.93	27.260	27.349	21.72	16.14	...
124.96	29.278	29.332	12.00	9.11	...

Col. 3 gives pressures corrected to the temperature chosen for the isotherm for each group of observations. Corrections of the vapor compositions to reduce them to isothermal conditions were entirely too small to be significant, except possibly at 90.5°K., where corrected values are given, though it is probable that the corrections are within the experimental error.

The pressure corrections were made with the aid of Raoult's law which leads to the following linear vapor-pressure relation

$$p = P_a x_1 + P_b(1 - x_1) \tag{1}$$

where p is the total vapor pressure, P_a the vapor pressure of pure A at the temperature in question, P_b the vapor pressure of pure B at the temperature in question and x_1 the mole fraction of A in the liquid phase.

Differentiation with respect to T at constant x_1 leads to the following correction equation.

$$\Delta p = \left[x_1 \frac{\Delta P_a}{\Delta t} + (1 - x_1) \frac{\Delta P_b}{\Delta t}\right] \Delta t \tag{2}$$

Raoult's law does not by any means hold exactly for this system but over the small ranges involved in making those corrections the assumption is quite allowable, as was shown by finding $(\partial p/\partial t)_{x_1}$ from the data at a number of points by a graphical method and the differences between these values and those calculated from Raoult's law were entirely negligible. Since the vapor-composition corrections are so small it is hardly worth while outlining the method used in obtaining them.

Interpolation of the Data.—In the study of the separation of binary systems by distillation and condensation, the following relations among the variables are particularly useful: (1) x_2 (mole fraction of oxygen in the vapor) as a function of x_1 (mole fraction of oxygen in the liquid) at constant p and at constant T; (2) p as a function of x_1 and x_2 at constant T; and (3) T as a function of x_1 and x_2 at constant p. Since there are four variables and two degrees of freedom, the system is completely represented by two equations, of which the following may be taken as typical

$$Z = f(p, T) \tag{3}$$

$$Z' = f'(x_1, T) \tag{4}$$

where Z and Z' may be either of the two variables not selected as independent variables or any combination of two, three or all four of the variables, the choice of a suitable function being dictated largely by convenience. As an example, for Z' the following two functions are useful, which will be designated as A and A', respectively,

$$[x_2(1 - x_1)]/[x_1(1 - x_2)] \tag{A}$$

and

$$[x_2(1 - x_1)P_b]/[x_1(1 - x_2)P_a] \tag{A'}$$

For the simplest case of binary solutions, the so-called "ideal" solution, A is a function of T only, or in other words, is constant at a given T, while $A' = 1$ for all values of T and x_1. For this particular system both A and A' are functions of both x_1 and T, and A was found to be somewhat the simpler to use. The general thermodynamic theory of binary mixtures leads to the following expression[15] for A

$$A = e^{\alpha + \beta x_1 + \gamma x_1^2 + \cdots} \tag{5}$$

where α, β, γ, etc., are functions of T. We have found this relation to hold

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[15] Kuenen, "Verdampfung und Verflüssigung von Gemischen," Leipzig, **1906**.

quite well for all the isotherms, generally with the use of only two constants, but the following simpler relation holds equally well and the constants can be more easily expressed as a function of T.

$$A = a + bx_1 + cx_1^2 + \dots \tag{6}$$

This relation has been applied to our data and to Inglis' data, and the constants, determined by the method of averages,[16] are given in Table II.

TABLE II

THE CONSTANTS OF EQUATION 6 AS A FUNCTION OF T

T	a	b	c
74.44	0.2535	−0.1141	0
79.11	.2804	− .1063	0
90.50	.3670	− .1093	0
99.94	.4432	− .1200	0
110.05	.5488	− .1644	0
119.92	.6723	− .2613	0.0605
125.00	.7861	− .4475	.1824

By plotting these constants against T, a relation of the form of Equation 4 is obtained. (No simple algebraic relation between the constants and T could be found, so the complete relation is partly algebraic and partly graphical.)

The relation just found is complete as far as x_1, x_2 and T are concerned, but does not involve the pressure. Another equation is necessary to determine the four variables. A very satisfactory equation is obtained by choosing for Z' in Equation 4 the function $(P_b - p)/[x_1(P_b - P_a)]$, which we shall designate as π.

For ideal solutions $\pi = 1$ for all values of x_1 and T. For this particular case it is a function of both x_1 and T but the maximum variation for all values of x_1 and T in our data and Inglis' data is only from 0.86 to 1.17. As x_1 approaches 1.00, π also approaches 1.00 in the general case, and this suggested the following simple relation between π and x_1

$$\pi = 1 + k(1 - x_1) + l\,(1 - x_1)^2 \tag{7}$$

where the last two terms are only small correction terms and k and l are functions of T only. The values of k and l determined by the method of averages are given in Table III.

TABLE III

CONSTANTS OF EQUATION 7 AS A FUNCTION OF T

T	k	l	T	k	l
74.44	−0.1913	0	110.00	0	0
79.11[a]	− .1633	0	119.92	0	+0.171
90.50	− .0993	0	125.00	0	+ .236
99.94	− .0587	0			

[a] In obtaining the value at $T = 79.11$, we have omitted three of Inglis' points which seem from the plot of π against x_1 to be inconsistent with the rest.

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[16] Lipka, "Graphical and Mechanical Computation," John Wiley and Sons, New York, 1918.

With the aid of Equation 6 and a graph of the constants against T and also Equation 7 with a similar graph, we may calculate the values of p and x_2 for any given values of T and x_1. The comparison between our observed isotherms and isotherms calculated in this way is given in Fig. 5. The lines are drawn through the calculated points and the points marked are the corrected observations. The isotherm at T = 75.00°K. is purely a calculated one.

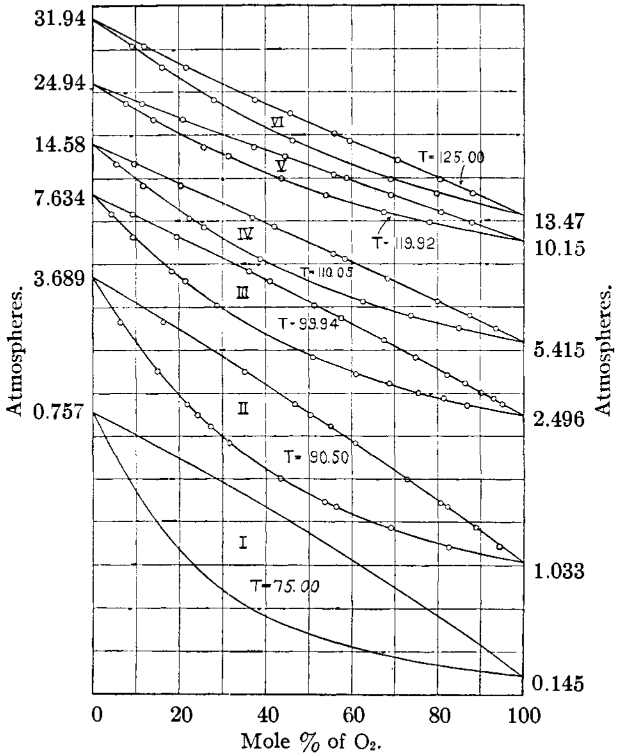

Fig. 5.—Isotherms of the system: oxygen-nitrogen. The curves are drawn through calculated points and the circles enclose observed points. Scale of pressures: one square (I) = 0.1 atm., (II) = 0.4 atm., (III) = 1.0 atm., (IV) = 2.0 atm., (V) = 4.0 atm., (VI) = 4.0 atm.

We may also obtain from our observations the vapor-pressure curves of the binary liquid mixtures. It was found that an equation of the form

$$\log_{10} p = B + C/T \qquad (8)$$

which holds quite well for most one-component liquid-vapor systems also holds very closely for this binary system at constant x_1 over the whole range of temperature. Since observations were not made at constant x_1 it was necessary to use Equation 7 for interpolation on each observed isothermal. In Table IV are given the values of the constants B and C for the binary mixtures along with the two obtained from the vapor-pressure equations of the two pure components.

TABLE IV

THE CONSTANTS OF EQUATION 8 AS A FUNCTION OF T

x_1	B	C	x_1	B	C
0	3.9335	−304.49	0.6	3.8444	−317.32
0.1	3.9051	−304.52	.7	3.8585	−323.89
.2	3.8818	−305.35	.8	3.8915	−333.18
.3	3.8626	−306.84	.9	3.9541	−346.64
.4	3.8493	−309.21	1.0	4.0630	−366.52
.5	3.8418	−312.52			

The agreement between pressures calculated from Equation 8 and the corresponding smoothed observations as obtained from Equation 7 is shown in Table V.

TABLE V

COMPARISON OF OBSERVED PRESSURES AND THOSE CALCULATED BY MEANS OF EQUATION 8

T = 90.50		T = 125.00	
p, calcd.	p, obs.	p, calcd.	p, obs.
3.469	3.444	29.44	29.74
3.220	3.197	27.48	27.69
2.966	2.944	25.58	25.76
2.708	2.687	23.75	23.93
2.446	2.425	21.96	22.16
2.178	2.156	20.22	20.44
1.904	1.884	18.51	18.74
1.622	1.607	16.83	17.03
1.330	1.324	15.17	15.28

The agreement is very good considering the approximate nature of Equation 8. Better agreement may, of course, be obtained by using three or four constants in Equation 8. The constants B and C when plotted against x_1 give a very smooth curve and from this plot and Equation 8 the temperature corresponding to any x_1 at any chosen constant pressure may be calculated. Then from the T and x_1, x_2 may be obtained from Equation 6. In this way a series of isopiestics up to and including p = 15.00 atm., was calculated and plotted in Fig. 6.

The function A, previously referred to, was found to be very nearly a constant along each isopiestic. From a plot of A against p, the value of A for any isopiestic is readily obtained and from this the vapor compositions. In this way the curve for 20 atmospheres was obtained.

Discussion of Results

The discussion of our results from the standpoint of the theory of binary solutions will be dealt with in a later paper. Likewise no attempt will be made here to show their application to practical problems of distillation and rectification, but we shall confine ourselves mainly to a comparison of our results with those of other observers.

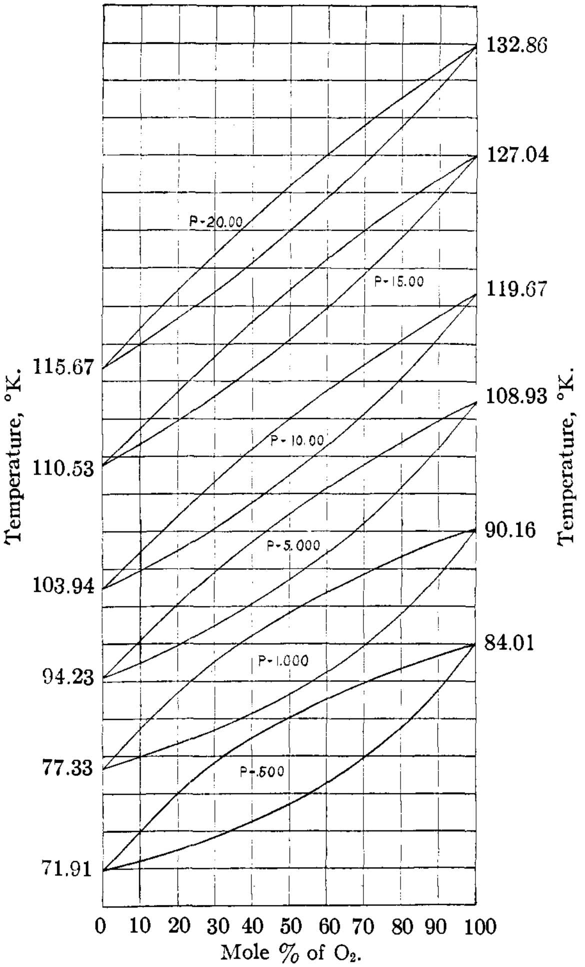

Fig. 6.—Isopiestics of the system: oxygen-nitrogen. Pressures are in atmospheres. Scale of temperatures: 1 square = 2°C.

As previously pointed out, we have made use of Inglis' results at temperatures below 90.5°K. to extrapolate our data. As a partial justification of this procedure there is given in Table VI a comparison between two measurements which we made in the region below 90.5°K. and the corresponding values calculated from the interpolation relations given above.

TABLE VI

COMPARISON BETWEEN THE TWO OBSERVATIONS BELOW 90 °K. AND VALUES CALCULATED BY THE INTERPOLATION EQUATIONS

T	P, obs.	P, calcd.	100 x_1	100 x_2, obs.	100 x_2, calcd.
76.79	0.600	0.602	49.15	16.62	17.02
77.36	.871	.894	15.86	4.59	4.74

The agreement is very satisfactory for data of this nature.

Kuenen and Clark's[17] measurements on the critical phenomena of air include one point low enough in temperature to come within the range of our measurements. The results they obtained at this point (123.00°K.) are given in Table VII in comparison with results calculated from our relations on the assumption that air contains 21.00% of oxygen and 79.00% of nitrogen.

TABLE VII

COMPARISON OF OUR DATA WITH THE RESULTS OF KUENEN AND CLARK ON AIR

	Dew point, atm.	End-point of condensation, atm.
Kuenen and Clark's observation	23.68	25.04
Calculated	23.52	25.00

The classical results in this field are those of Baly.[1a] Although none of our observations were made at a pressure of 1 atmosphere (Baly's results are all for $p = 1$ atm.) we may calculate from our interpolation relations the vapor compositions and temperatures corresponding to Baly's liquid compositions at a constant pressure of 1 atmosphere. The comparison is given in Table VIII.

TABLE VIII

COMPARISON OF OUR RESULTS WITH THOSE OF BALY

100 x_1	Temp., °K. (Baly)	Temp., °K. (Dodge and Dunbar)	100 x_2 (Baly)	100 x_2 (Dodge and Dunbar)
0	77.54	77.35	0	...
8.10	78.00	77.86	2.18	2.30
21.60	79.00	78.78	6.80	6.50
33.35	80.00	79.72	12.00	11.05
43.38	81.00	80.65	17.66	15.65
52.17	82.00	81.60	23.60	21.05
59.53	83.00	82.48	29.95	26.26
66.20	84.00	83.38	36.86	32.05
72.27	85.00	84.28	44.25	38.40
77.80	86.00	85.22	52.19	45.80
82.95	87.00	86.18	60.53	54.00
87.60	88.00	87.15	69.58	63.40
91.98	89.00	88.14	79.45	73.90
96.15	90.00	89.18	89.80	86.03
100.00	90.96	90.17	100.00	100.00

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[17] Kuenen and Clark, *Comm. Phys. Lab. Leiden*, No. 150, 1919.

Baly's temperature scale is obviously considerably in error in view of the accuracy with which the boiling points of the two pure components are now known. The discrepancy between the vapor compositions is considerable but is not surprising in view of the method which Baly used. This is not to be taken as a disparagement of Baly's work, which was the pioneer work in this field and has been of great value in the large-scale development of air separation, but it merely means that an improved technique has presumably given more accurate results. Furthermore, he took no steps to remove argon which would affect his results to a small extent, but could not possibly account for the above discrepancy.

In Table IX is given a comparison between results obtained by Dunbar and Davis[4] using the method previously referred to as the Dunbar method, and corresponding results calculated from our interpolation relations.

TABLE IX

COMPARISON OF OUR RESULTS WITH UNPUBLISHED OBSERVATIONS OF DUNBAR AND DAVIS

Temp., °K.	100 x_1	100 x_2 (Dunbar and Davis)	100 x_2 (Dodge and Dunbar)	P, atm. (Dunbar and Davis)	P, atm. (Dodge and Dunbar)
90.58	92.13	75.08	75.70	1.262	1.278
90.61	88.14	68.80	66.80	1.392	1.394
97.41	88.10	69.55	70.15	2.590	2.560
103.60	86.24	69.02	69.45	4.246	4.282
108.29	86.04	70.23	70.90	5.908	5.975
108.36	86.70	73.45	72.10	6.101	5.952
112.33	84.92	70.86	70.70	7.775	7.880
114.79	82.69	69.50	68.55	9.254	9.232
118.21	83.44	71.69	71.00	11.18	11.40
120.95	82.16	70.76	70.00	13.20	13.46
122.69	81.30	70.48	69.30	14.53	14.90
124.51	81.23	70.82	69.95	16.15	16.41

The agreement is not as good as might be desired, yet it is probably as close as is generally obtained in this field. It should also be considered that Dunbar and Davis used total evaporation for obtaining their liquid samples and that their temperature scale was based on only two fixed points, the highest of which was 90°K.

The most striking characteristic of the data, when presented in graphical form, is the steady decrease in spread between liquid and vapor compositions that takes place as the temperature or pressure is increased, a result that would be expected on the general ground that as the critical region is approached the vapor and liquid tend to become identical.

We wish to express our appreciation to Professor H. N. Davis of the Harvard Engineering School, under whose general direction the work was done, and also to the Air Reduction Company of New York for financial assistance.

Summary

A method for the study of liquid-vapor phase equilibria in binary solutions of oxygen and nitrogen has been described. Results of the measurement of pressure, liquid-phase composition and vapor-phase composition at a series of constant temperatures from 90°K. to 125°K. are tabulated. These data combined with earlier data of Inglis for lower temperatures are then utilized in the development of interpolation relations. The calculated results for a constant pressure of 1 atmosphere call for a considerably greater spread between liquid and vapor compositions than is given by the classical results of Baly.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CRYOGENIC ENGINEERING LABORATORY OF HARVARD UNIVERSITY]

VAPOR PRESSURE OF LIQUID OXYGEN AND NITROGEN

BY BARNETT F. DODGE AND HARVEY N. DAVIS

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Introduction

In connection with an investigation of the binary system: oxygen-nitrogen at low temperatures, the opportunity was afforded of measuring the vapor pressure of liquid oxygen from a pressure of about 0.2 to 21 atmospheres, and of liquid nitrogen from the normal boiling point to the critical point.

Previous Investigations

Oxygen vapor pressures have been measured by Wroblewski,[1] Olszewski,[2] Estreicher and Olszewski,[3] Baly,[4] Travers, Senter and Jaquerod,[5] Bestelmeyer,[6] Onnes and Braak,[7] Germann,[8] Bulle,[9] Von Siemens,[10] Henning,[11] Onnes, Dorsman and Holst,[12] Cath,[13] Keyes, Townshend and Young,[14] and Henning and Heuse.[15]

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[1] Wroblewski, *Compt. rend.*, **98**, 982 (1884); *Sitzb. Akad. Wiss. Wien*, **91**, 705 (1885).

[2] Olszewski, *Compt. rend.*, **100**, 350 (1885).

[3] Estreicher and Olszewski, *Phil. Mag.*, [5] **40**, 454 (1895).

[4] Baly, *ibid.*, [5] **49**, 517 (1900).

[5] Travers, Senter and Jaquerod, *Proc. Roy. Soc.*, **70**, 484 (1902).

[6] Bestelmeyer, *Ann. Physik.* **14**, 87 (1904).

[7] Onnes and Braak, *Comm. Leiden*, 107a, **1908**.

[8] Germann, *Physik. Z.*, **14**, 857 (1913).

[9] Bulle, *ibid.*, **14**, 860 (1913).

[10] Von Siemens, *Ann. Physik*, **42**, 871 (1913).

[11] Henning, *ibid.*, **43**, 289 (1914).

[12] Onnes, Dorsman and Holst, *Comm. Leiden*, 145b, **1914**.

[13] Cath, *ibid.*, 152d, **1918**.

[14] Keyes, Townshend and Young, *J. Math. Phys. Mass. Inst. Tech.*, **1**, 243 (1922).

[15] Henning and Heuse, *Z. Physik*, **23**, 105 (1924).