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NATIONAL DEFENSE RESEARCH COMMITTEE
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OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

VAPOR-LIQUID EQUILIBRIUM FOR THE SYSTEM OXYGEN-NITROGEN-ARGON

to
December 7, 1944
by
M. L. Sagenkahn and H. L. Fink

Report OSRD No. 4493
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Division 11
NATIONAL DEFENSE RESEARCH COMMITTEE
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Section 11.1

VAPOR-LIQUID EQUILIBRIUM FOR THE SYSTEM OXYGEN-NITROGEN-ARGON

Service Directives: AC-12; NA-111; NS-115; NS-116; CE-29

Endorsement (1) From E. P. Stevenson, Chief, Division 11 to Dr. Irvin Stewart, Executive Secretary of the National Defense Research Committee.

Forwarding report and noting:

> "This report is final with respect to that portion of the work under this contract relating to Vapor-Liquid Equilibrium for the System O_2 - N_2 - A. The following OSRD reports cover information on other subjects investigated under this contract, Nos. 3482, 3483, 3484, 3524, 3699. Part of the work for this present report was completed at the University of Pennsylvania under contract OEMsr-984."

This is a final report under Contract 11-307, OEMsr-685 with the Pennsylvania State College.

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Final Report

Vapor-Liquid Equilibrium for the System Oxygen-Nitrogen-Argon

Contract OEMsr-685
School of Chemistry and Physics
The Pennsylvania State College

Contract OEMsr-934
The Central Engineering Laboratory
University of Pennsylvania

Prepared by Malcolm L. Sagenkahn
Herman L. Fink
The Pennsylvania State College

J. G. Aston

Submitted by J. G. Aston
Official Investigator,
Contract OEMsr-685
Consultant
Contract OEMsr-934

December 7, 1944

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Final Report On

VAPOR-LIQUID EQUILIBRIUM FOR THE SYSTEM

OXYGEN-NITROGEN-ARGON

Abstract

The application of the Duhem equation to the data on binary systems is discussed.

All the available equilibrium data for the two component systems of oxygen-nitrogen-argon mixtures have been summarized and have been tested for their reliability by means of the Duhem equation.

The apparatus and method used for measurements of the liquid-vapor equilibria in the system oxygen-argon are described. This was an apparatus for thermal data on condensed gases already in the laboratory.

Complete vapor-liquid equilibrium data for the system argon-oxygen at one atmosphere pressure over the entire range of composition have been obtained.

Vapor pressures for argon-oxygen mixtures over the entire composition range and at pressures ranging from 550 to 850 mm. of Hg. have been determined and equations calculated for them.

The accuracy of the above data on the system argon-oxygen was tested using the Duhem equation.

An apparatus for obtaining liquid-vapor equilibria by a static method which comes to equilibrium rapidly has been developed.

An analytical procedure for determining compositions of oxygen-nitrogen-argon mixtures has been developed.

Sample data obtained during an equilibrium measurement are given.

Abstract
(con't.)

Data for the systems argon-oxygen, nitrogen-oxygen and oxygen-nitrogen-argon to two atmospheres pressure have been obtained using the new equilibrium apparatus.

Three equilibrium measurements on the argon-oxygen system were made in the new apparatus to check the approach to equilibrium in the old apparatus.

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FIGURES
(con't.)

INTRODUCTION

The limitations imposed on the size of the portable oxygen units needed by the armed forces have necessitated very careful designing of the fractionating towers. The present report presents reliable and consistent data on the equilibrium of binary and ternary mixtures of oxygen, nitrogen and argon. By the application of these equilibrium data to results obtained in pilot plant size air rectification columns, it should be possible to predict the type and dimensions of tower to perform any given separation.

In order that none of the available results on liquid vapor equilibrium of the air system be needlessly repeated, a survey of all work available has been made and is summarized in the next section.

Available Data

Nitrogen-Oxygen Work on this system has been done by Baly[1], Inglis[2], and Dodge and Dunbar[3]. Baly's measurements were taken by a static method at one atmosphere only. Inglis' measurements were taken along two isotherms, namely at 74.7°K (-325.3°F) and at 79.07°K (-319.2°F), by a circulation method. The investigation of Dodge and Dunbar constitutes perhaps the most complete set of data on any system in this type of work, extending from pressures below 1 atmosphere up to nearly the critical pressure of nitrogen, corresponding to a temperature range from 77°K (-321°F) to 125°K (-235°F). Their measurements were taken by a circulation method.

Figure 1 is a plot of $K = y/x$ = mole fraction nitrogen in the vapor/mole fraction nitrogen in the liquid versus x for the data of Dodge and Dunbar at 1, 2, 5, and 10 atmospheres total pressure.

Argon-Oxygen Data on this system have been presented by Bourbo and Ishkin[4], and Shilling[5]. The measurements of Bourbo and Ishkin, which were taken by the boiling point method extend over three isotherms at 87°K (-302°F), 90°K (-297.8°F), and 95°K (-288.9°F). Their data were also interpolated for isobars at 1, 1.4, and 2 atmospheres. Shilling's data, which he states are of "only engineering accuracy", were taken by a static method at one atmosphere only.

Figure 2 is a plot of $K = y/x$ = mole fraction argon in the vapor/mole fraction argon in the liquid versus x for the data of Bourbo and Ishkin at 1 and 2 atmospheres and for the data of Shilling at 1 atmosphere.

Argon-Nitrogen The only available data on this system were taken using the boiling point method by Holst and Hamburger[6]. Their measurements extend over four isobars at 500, 760, 1000, and 1500 mm (or 9.7, 14.7, 19.3 and 29.0 lbs. per sq. in., respectively) and one isotherm at 85.11°K (-306.5°F).

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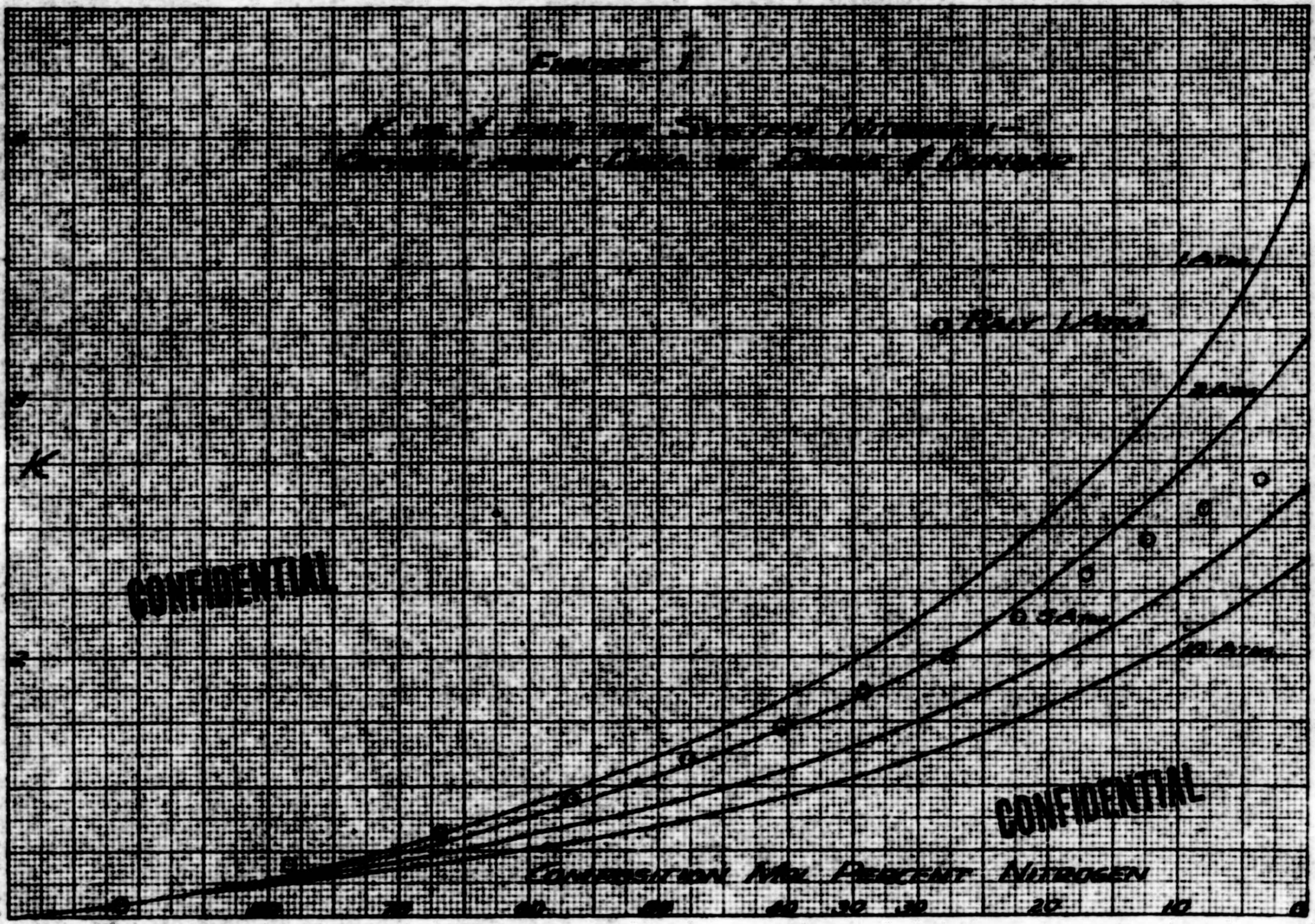

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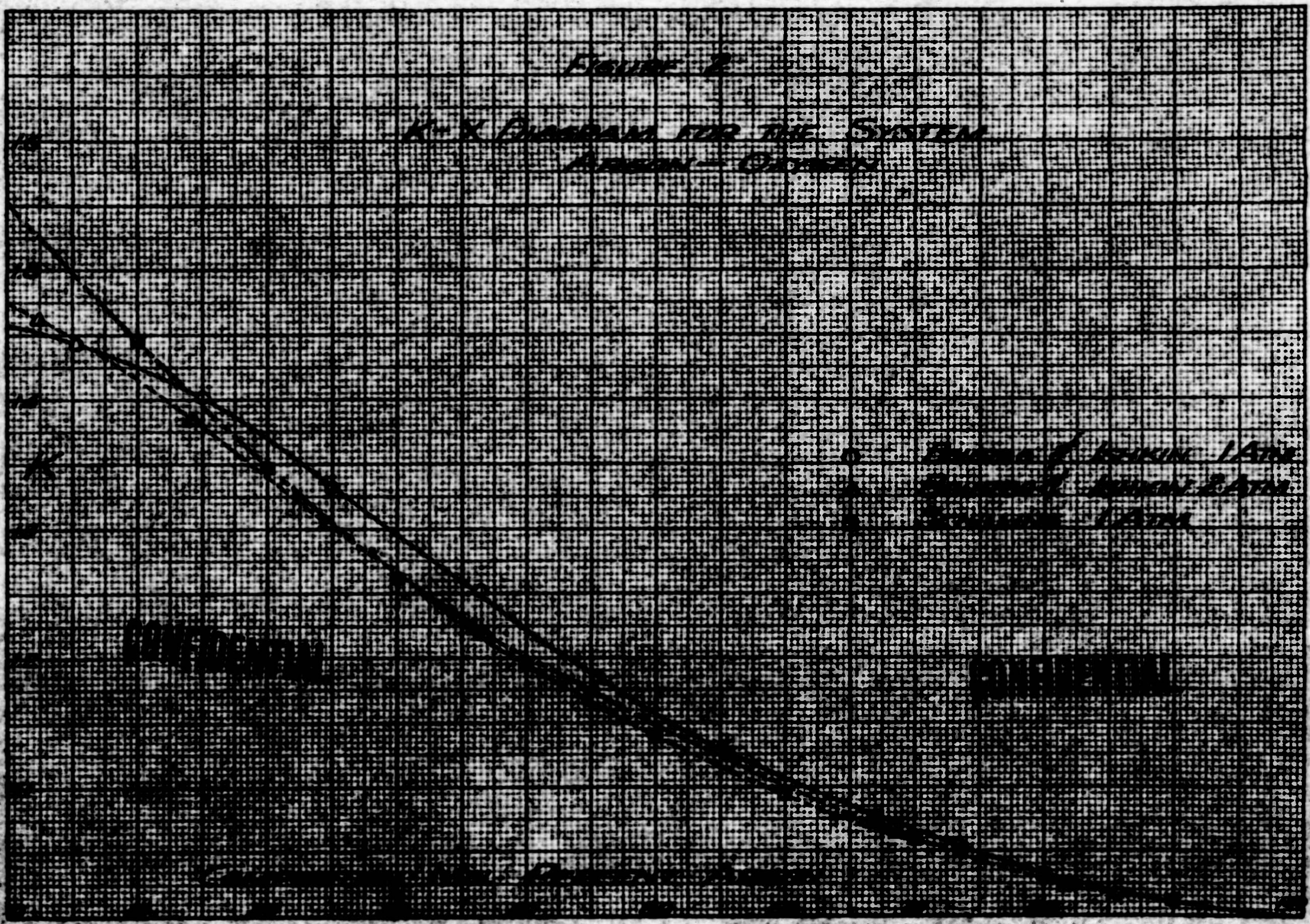

Figure 2

K–X Diagram for the System
Argon – Oxygen

2 b

Figure 3 is a plot of $K = y/x$ = mole fraction argon in the vapor/mole fraction argon in the liquid versus x for their data at one and two atmospheres. Oxygen-Nitrogen-Argon The only available data on the three component system were taken, using the flow method, by Torochesnikov and Ershova[7].

Figures 4, 5, 6, and 7 are the triangular phase diagrams representing the data of Torochesnikov and Ershova on the ternary system and are included for completeness. The end points for the two component systems (as selected from available data) have also been added to these points as an aid in orienting the curves.

Their data cover the triangular phase diagrams at a temperature of 90.1°K (-297.6°F) and at pressures of 1.5 Kgm/cm^2, 2.5 Kgm/cm^2, 5.0 Kgm/cm^2, and 10 Kgm/cm^2.

With the compilation of all available data on the air system, it remains to evaluate these data as to their reliability. A cursory glance at the data shows several inconsistensies. The data of Bourbo and Ishkin on the argon-oxygen system show an increase in the separation of the liquid and vapor curves with pressure over parts of the concentration range. This seems extremely unlikely in view of the small deviation of this mixture from Raoults law and the nature of the vapor pressure equations for pure argon and pure oxygen. Another inconsistency is the obvious discrepancy between the points of the triple system data of Torochesnikov and Ershova presented in figures 4, 5, 6 and 7, and the end points for this system as selected from the available two component date.

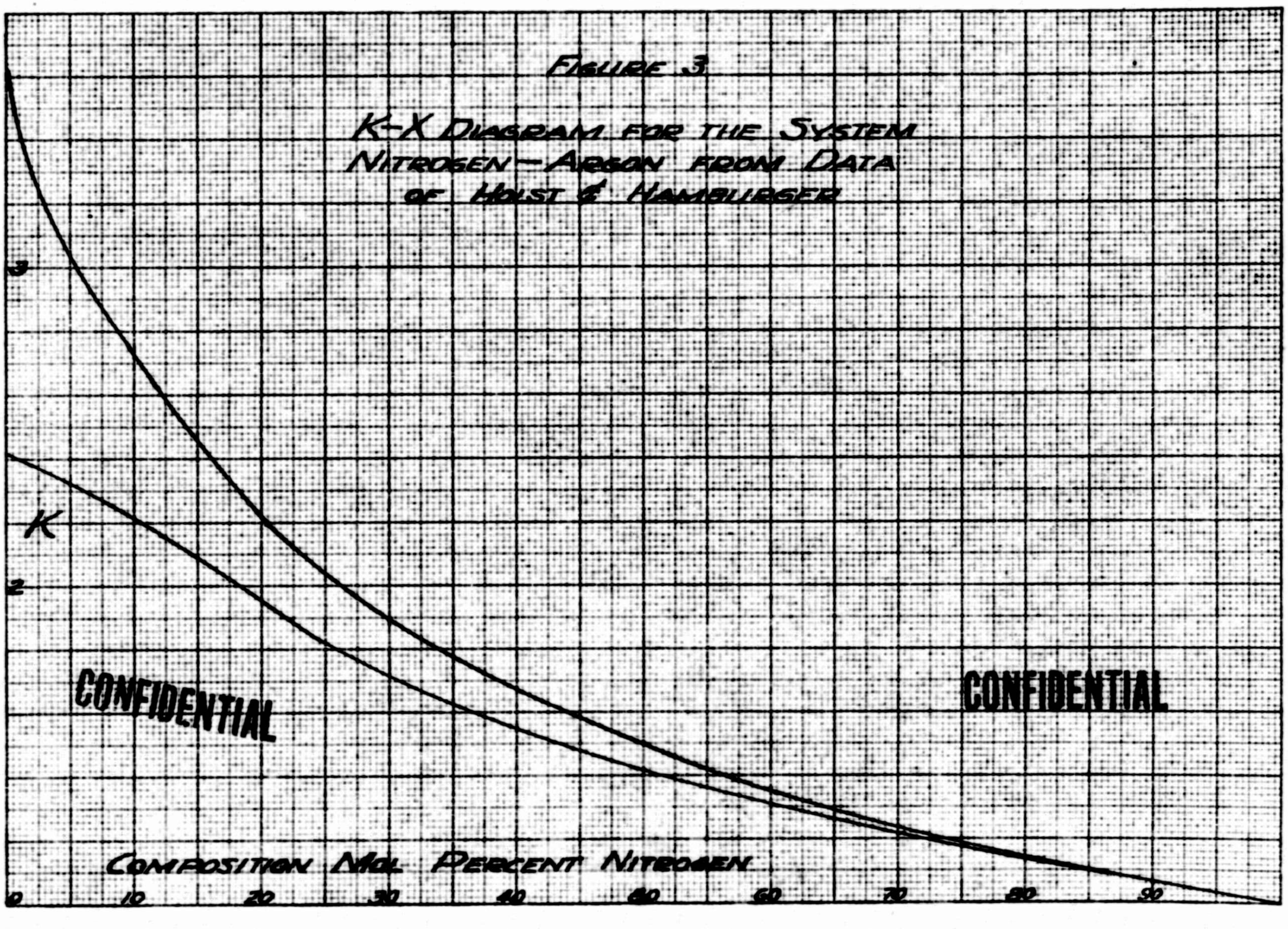

FIGURE 3

K-X DIAGRAM FOR THE SYSTEM NITROGEN – ARGON FROM DATA OF HOLST & HAMBURGER

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FIG. 4

EQUILIBRIUM DIAGRAM FOR
N_2-A-O_2 AT 90.1°K 1.45 ATM.
FROM DATA OF
TORQCHNESHNIKOV & ERSHOVA

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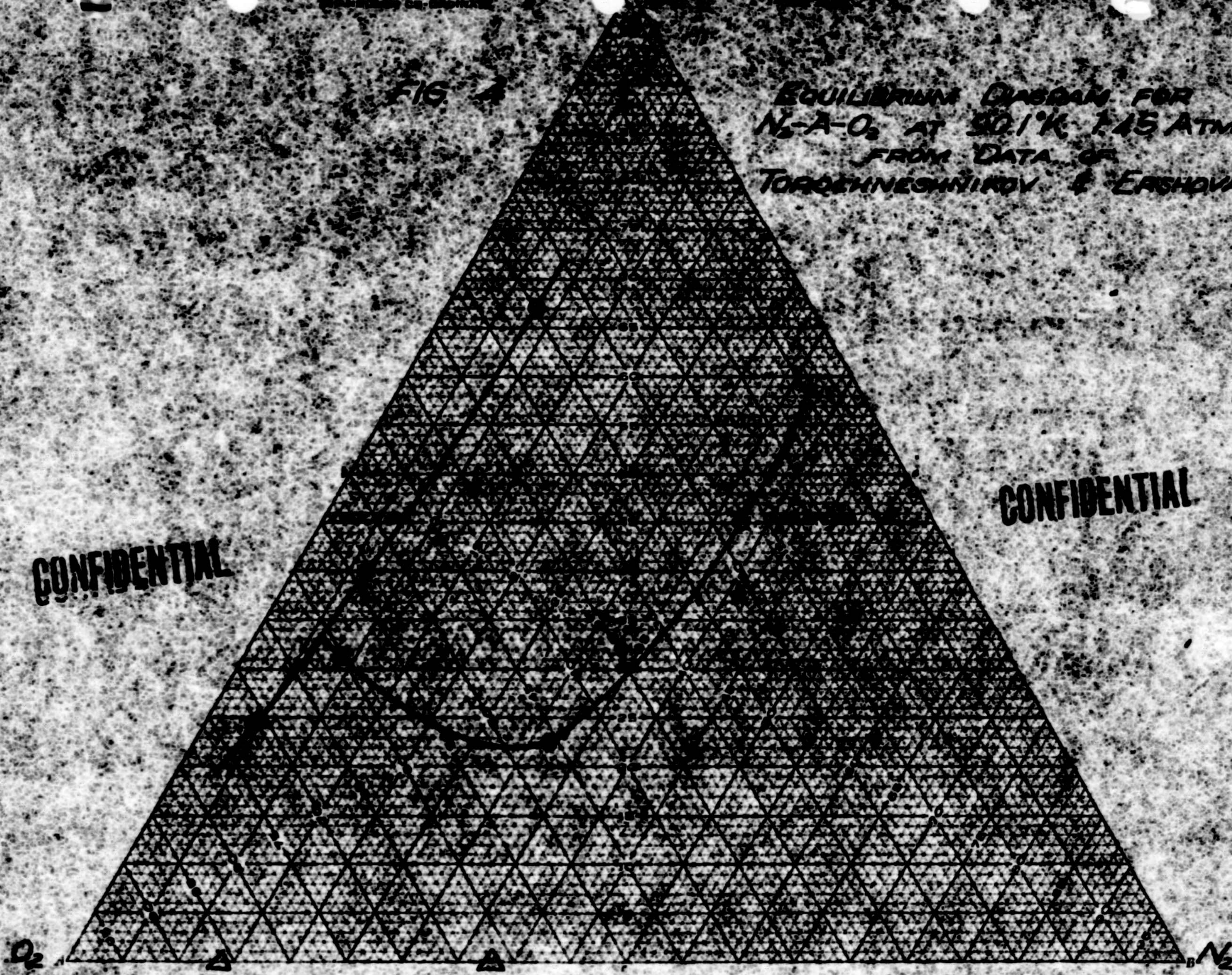

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FIG. 5

Equilibrium Diagram for
N-A-O_2 at 921°K. & 42 Atm
from Data of
Jorochneshnikov & Ershova

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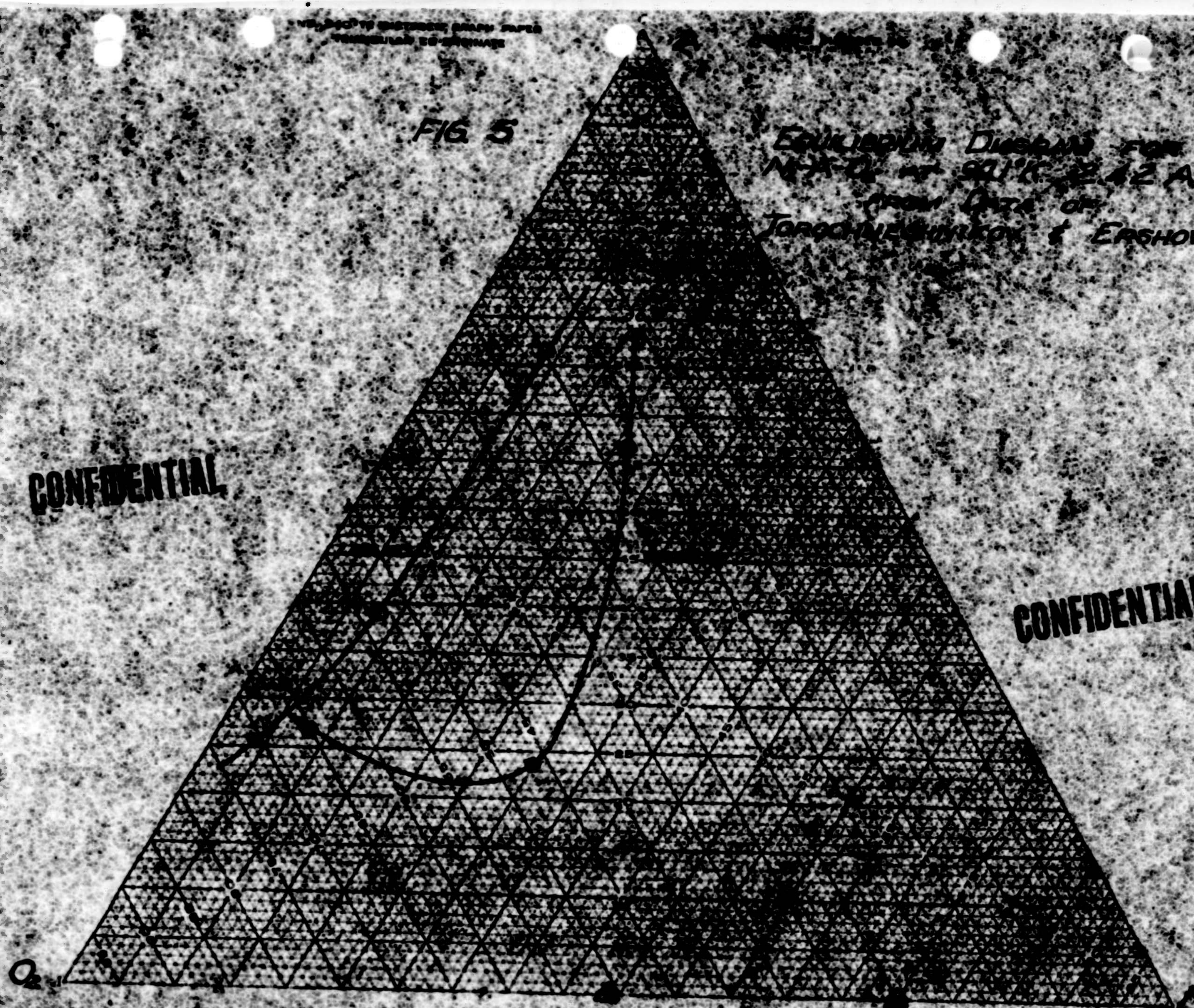

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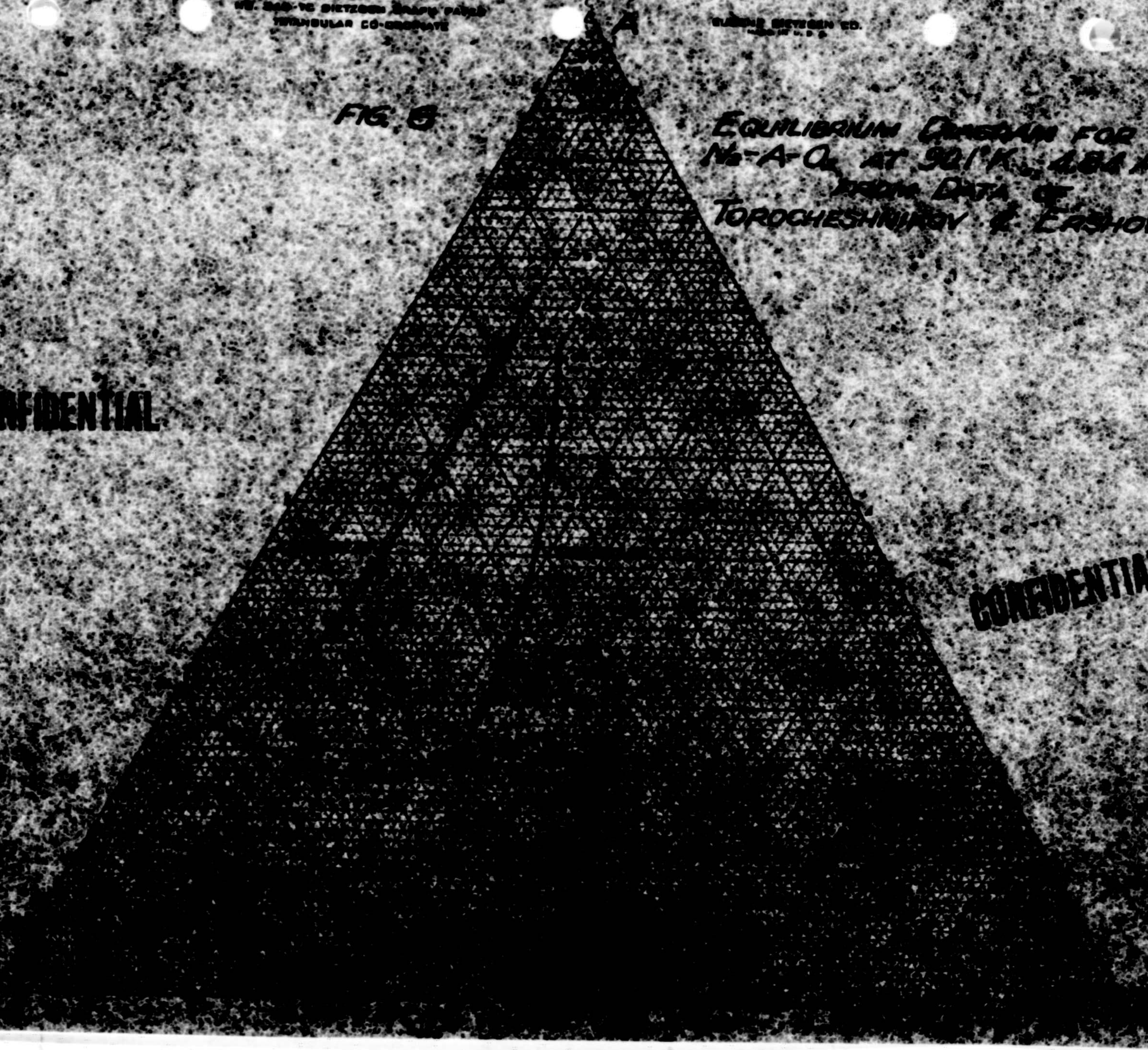
FIG. 8



EQUILIBRIUM DIAGRAM FOR
N_2-A-O_2 AT 90.1°K., 4.84 ATM
FROM DATA OF
TOROCHESHNIKOV & ERSHOVA

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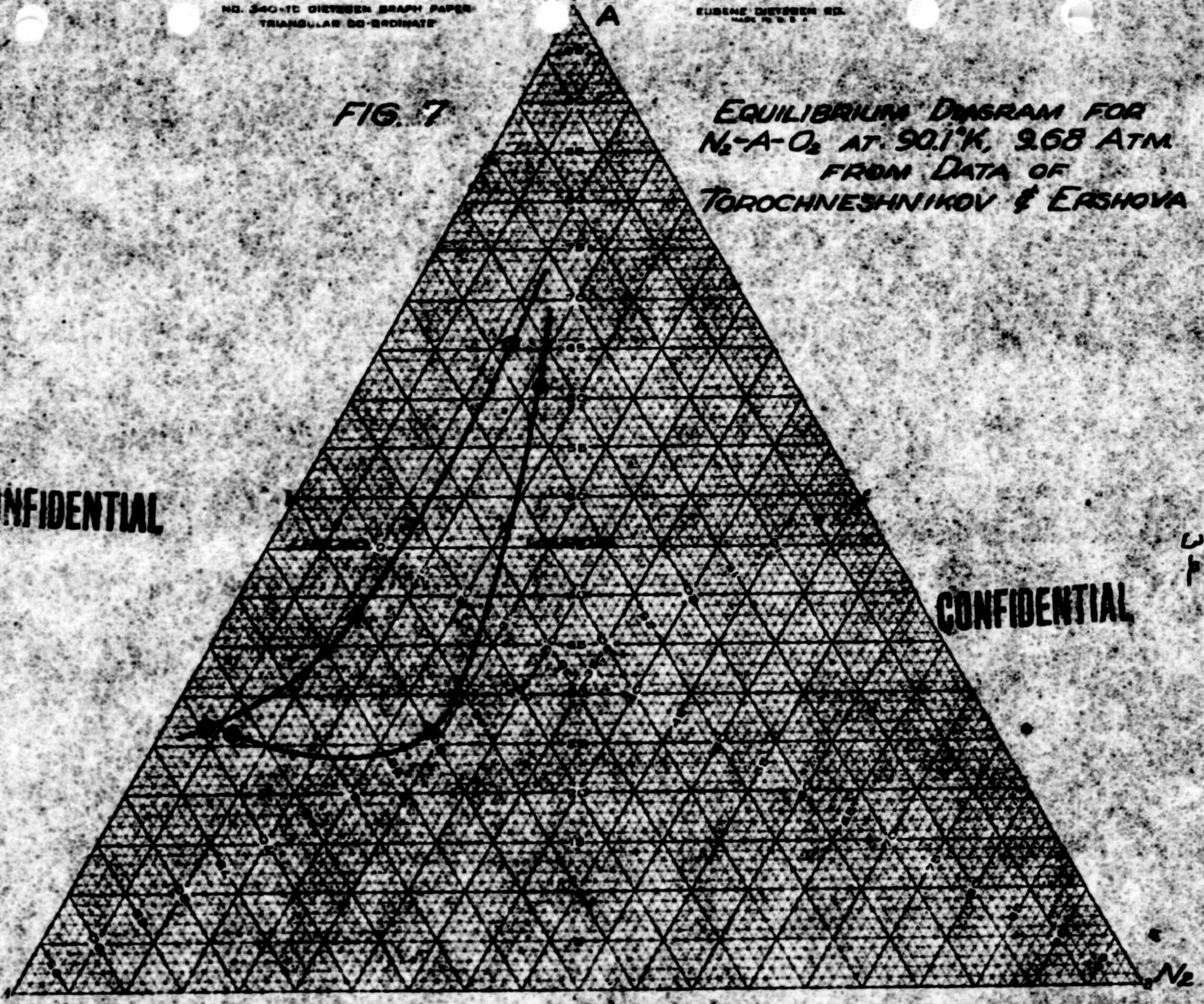
3p

FIG. 7



EQUILIBRIUM DIAGRAM FOR
N_2-A-O_2 AT 90.1°K, 2.68 ATM.
FROM DATA OF
TOROCHNESHNIKOV & ERSHOVA

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The Application of the Duhem Equation to the Data on Binary Systems

In order to test the accuracy of the available data, the activities of one component have been calculated from those of the other and compared with the values derived directly from the equilibrium partial pressure. This is simply the application of the Duhem equation in the proper manner.

The Duhem equation expressed in its most general form is

$$\sum N_1 dF_1 = 0 \quad \ldots\ldots (1)$$

for a two phase system this reduces to

$$N_1 dF_1 + N_2 dF_2 = 0 \quad \ldots\ldots (2)$$

and since $dF = R\,T\,d \ln a$ . . . . . . (3)

$$\text{then } d \ln a_1 = -\frac{N_2}{N_1}\, d \ln a_2 \quad \ldots\ldots (4)$$

$$\text{or } \log \frac{a_1}{a_1^{1}} = -\int_{N_2^{1}}^{N_2} \frac{N_2}{N_1}\, d\log a_2 \quad \ldots\ldots (5)$$

it can be very easily shown that this can be transformed to

$$\log \frac{a_1}{N_1} = -\int_{0}^{N_2} \frac{N_2}{N_1}\, d \log \frac{a_2}{N_2} \quad \ldots\ldots (6)$$

For a solute $a_2/N_2 = 1$ as $N_2 \longrightarrow 0$ also $a_2 \propto f_2$

and as we pass from a mol fraction N_2 to an infinitely dilute solution $N_2{}^*$

$$\frac{a_2}{f_2} = \frac{a_2^*}{f_2^*} \quad \ldots\ldots (7)$$

from Henry's Law $\frac{N_2}{f_2}$ approaches a constant value at infinite dilution denoted by $\frac{N_2^*}{f_2^*}$.

But by definition $N_2^* = a_2^*$

$$\text{thus } a_2 = f_2 \frac{N_2^*}{f_2^*} \text{ and } \frac{a_2}{N_2} = f_2/N_2 \big/ f_2^*/N_2^* \quad \ldots\ldots (8)$$

If the solute forms a perfect gas, f_2 and f_2^* may be replaced by the corresponding partial pressures.

For the solvent, by definition:

$$\frac{a_1}{N_1} = 1 \text{ when } N_1 = 1$$

$$a_1 = \frac{f_1}{f_1^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

or if the gas is perfect

$$a_1 = \frac{p_1}{p_1^0}$$

In the case of the air system even at pressures as low as 1 atmosphere it is not justifiable to neglect gas imperfections.

Fortunately, the calculation of the fugacity from the actual pressure can be performed simply when the deviations are small as is true in the present case. For any gas whose volume is given by

$$V = RT/P - \alpha(T,P) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

where $\alpha(T,P)$ = a function of T and P

$$\log \gamma = -1/2.303RT \int_0^P \alpha(T,P)\, dP \quad \ldots\ldots\ldots \quad (11)$$

where $\gamma = f/P \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (12)$

The integral can be obtained either graphically or analytically when state data are available.

According to Lewis[8], in calculating fugacities corresponding to the partial pressures of a gas mixture, it can be assumed that the ratio of the fugacity to the partial pressures is equal to the ratio of the fugacity of the pure component to its pressure at a pressure equal to the total pressure of the gas mixture.

In the absence of state data, it is convenient to use the modified Berthelot equation of state if values of γ are desired at moderate pressures

($<$ 10 atm). This equation is

$$PV = RT \left[1 + 9PT_c(1 - 6T_c^2/T^2)/128P_cT\right] \ldots\ldots\ldots \quad (13)$$

and the corresponding value of $\alpha(T,P)$ is

$$\alpha(T,P) = -\frac{9RT_c(1 - 6T_c^2/T^2)}{128P_c} \ldots\ldots\ldots\ldots\ldots \quad (14)$$

Substitution of equation (14) in (11) and integration gives

$$2.303 \log \gamma = \left[(9/128)\ (T_c/P_cT) - (27/64)\ (T_c^3/P_cT^3)\right] P \ldots\ldots \quad (15)$$

All the data listed in the previous summary to which the Duhem equation can be applied have been examined. This test must be applied to data taken at constant temperature for this is assumed in the derivation of the Duhem equation itself. The results of these tests are listed in Tables I - III.

Table I gives the values of a_1 calculated from equation (9) (col. 2) and also the values of a_1 calculated from equation (6) (col. 3) for the data of Dodge and Dunbar on the N_2-O_2 isotherm at 90.50°K; while Table II is for the data of Inglis on the N_2-O_2 isotherms at 74.70°K and 79.07°K calling nitrogen the solvent (N_1) and oxygen the solute (N_2). All fugacities were calculated from equation (15) using the following critical constants

for nitrogen

T_c = -147.1°C = 126.1°K
P_c = 33.5 atm.

for oxygen

T_c = -118.8°C = 154.4°K
P_c = 49.7 atm.

The comparison shows that both sets of data are excellent.

Table III is a similar table for the data of Holst and Harburger on an A-N_2 isotherm at 85.11°K. Argon in this case is called the solvent and nitrogen the solute. As in the case of table I, the fugacities were calculated

TABLE I

DODGE AND DUNBAR

N_2-O_2 isotherm at 90.50°K.

N_1 (N_2)	$a_1 = f_1/f_1^o$	a_1 (plot)	Percent Dev.
0.99	0.9893	0.9900	-0.07
0.98	0.9793	0.9800	-0.07
0.95	0.9490	0.9520	-0.32
0.90	0.8972	0.9019	-0.52
0.85	0.8482	0.8558	-0.89
0.80	0.8004	0.8178	-2.13
0.70	0.7080	0.7159	-1.10
0.60	0.6139	0.6167	-0.45
0.50	0.5191	0.5205	-0.27
0.40	0.4239	0.4272	-0.77
0.30	0.3231	0.3329	-2.94
0.20	0.2231	0.2401	-7.05
0.10	0.1128	0.1089	+3.58

TABLE II

INGLIS

$N_2 - O_2$ isotherm at 74.70°K				$N_2 - O_2$ isotherm at 79.07°K			
N_1 (N_2)	$a_1 = {}^{f}1/f_1{}^{o}$	a_1 (plot)	Percent Dev.	N_1 (N_2)	$a_1 = {}^{f}1/f_1{}^{o}$	a_1 (plot)	Percent Dev.
0.99	0.9896	0.9902	-0.06	0.99	0.9911	0.9900	+0.11
0.98	0.9792	0.9805	-0.13	0.98	0.9816	0.9804	0.12
0.95	0.9494	0.9543	-0.51	0.95	0.9538	0.9510	0.29
0.90	0.9036	0.9099	-0.69	0.90	0.9073	0.9014	0.65
0.85	0.8583	0.8656	-0.85	0.85	0.8585	0.8516	0.81
0.80	0.8132	0.8212	-0.98	0.80	0.8090	0.8024	0.82
0.70	0.7236	0.7321	-1.16	0.70	0.7141	0.7076	0.91
0.60	0.6339	0.6417	-1.22	0.60	0.6234	0.6187	0.76
0.50	0.5410	0.5414	-0.08	0.50	0.5341	0.5251	1.77
0.40	0.4465	0.4457	+0.02	0.40	0.4392	0.4269	2.80
0.30	0.3463	0.3379	+3.53	0.30	0.3380	0.3282	2.88
0.20	0.2389	0.2316	+3.18	0.20	0.2338	0.2232	4.53
0.10	0.1271	0.1408	+9.74	0.10	0.1213	0.1194	1.59

6 f

TABLE III

HOLST AND HAMBURGER

$A - N_2$ isotherm at 85.11°K

N_1 (A)	$a_1 = f_1/f_1^0$	a_1 (plot)	Percent Dev.
0.99	0.9907	0.9900	+0.07
0.98	0.9802	0.9800	0.02
0.95	0.9489	0.9500	-0.12
0.90	0.9014	0.9020	-0.07
0.80	0.8101	0.8107	-0.08
0.70	0.7249	0.7212	+0.51
0.60	0.6347	0.6274	1.15
0.50	0.5385	0.5299	1.60
0.40	0.4429	0.4305	2.82
0.30	0.3496	0.3309	5.34
0.20	0.2429	0.2246	7.53
0.10	0.1249	0.1138	8.90

from equation (15) using the critical constants for nitrogen as given above and for argon

$$T_c = -122.0^{\circ}C = 151.2^{\circ}K$$

$$P_c = 48 \text{ atm.}$$

The data of Bourbo and Ishkin were not evaluated in this manner for they calculated their results from the Gibbs-Duhem equation and this would constitute merely a check on their calculations.

The results of the literature survey on the air system and subsequent evaluation of this data show the need for the following data:

(1) The Argon-Oxygen system should be reinvestigated at total pressures from 1 to 2 atm. and in the concentration range from 0 to 50 mol% argon in the liquid because of the inconsistencies in Bourbo and Ishkin's data at the higher pressures.

(2) The Oxygen-Nitrogen-Argon system should be investigated at total pressures from 1 to 2 atm. over the entire concentration range of oxygen and nitrogen and from 0 - 20 mol% argon in the liquid.

(3) The Nitrogen-Oxygen system should be reinvestigated at total pressures from 1 to 2 atm. and over the entire concentration range, as part of the work on the ternary system, the data of Dodge and Dunbar having been shown sufficiently reliable to serve as a check.

In addition to the above, the remaining data needed to complete the air system (up to the critical region) are desirable.

Part II of this report gives the results of the investigation of the Oxygen-Argon system at 1 atmosphere over the entire range of concentration.

Part III gives the results of the investigation of:

(1) The Argon-Oxygen system at 2 atmospheres and from 0 to 50 mol% argon in the liquid,

(2) The Nitrogen-Oxygen system from 1 to 2 atmospheres over the entire range of concentration,

(3) The Oxygen-Nitrogen-Argon system from 1 to 2 atmospheres at concentrations that have appeared in plate calculations made on towers tested at the Pennsylvania State College.

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VAPOR-LIQUID EQUILIBRIUM DATA FOR THE SYSTEM ARGON OXYGEN AT ONE ATMOSPHERE PRESSURE OVER THE ENTIRE RANGE OF COMPOSITION

Apparatus:

The laboratory isothermal calorimeter,[9] C, was used for these measurements. For temperature measurements, gold resistance thermometer R-100 and standard thermocouples S-7 and S-4 were used. These had been checked against vapor pressures of pure oxygen in October 1941. The resistance thermometer R-100 was compared against thermocouples S-4 and S-7 during every run. The manometric mercury levels were measured by a Societe Genevoise cathetometer, with two telescopes with micrometer eye-pieces, which could detect differences of 0.001 mm. This instrument was used to compare the mercury height with lengths on a standard meter which had been calibrated by the U. S. Bureau of Standards. The pressure determinations were thus accurate to 0.02 mm. of mercury.

The relationship of the calorimeter to the auxiliary lines is shown in Figure 9. The three liter and 0.2 liter bulbs had graduated capillaries and were calibrated gravimetrically with both mercury and water to an accuracy of 0.1 and 0.01 cc. respectively. The line volumes, which are smaller, were determined by measurement of the pressure after expansion from a calibrated bulb at a known pressure into the volume to be determined, which had been first evacuated. The line volumes were known to 0.2 per cent in all cases. The three liter and 0.2 liter bulbs were placed in a thermostat, the temperature of which was kept constant to "0.002°C." as determined by a Beckmann thermometer. The absolute temperature of the latter was ascertained by reference to a Coloz thermometer graduated in intervals of 0.02°C. which had been calibrated by the Bureau of Standards and was accurate to within 0.01°C.

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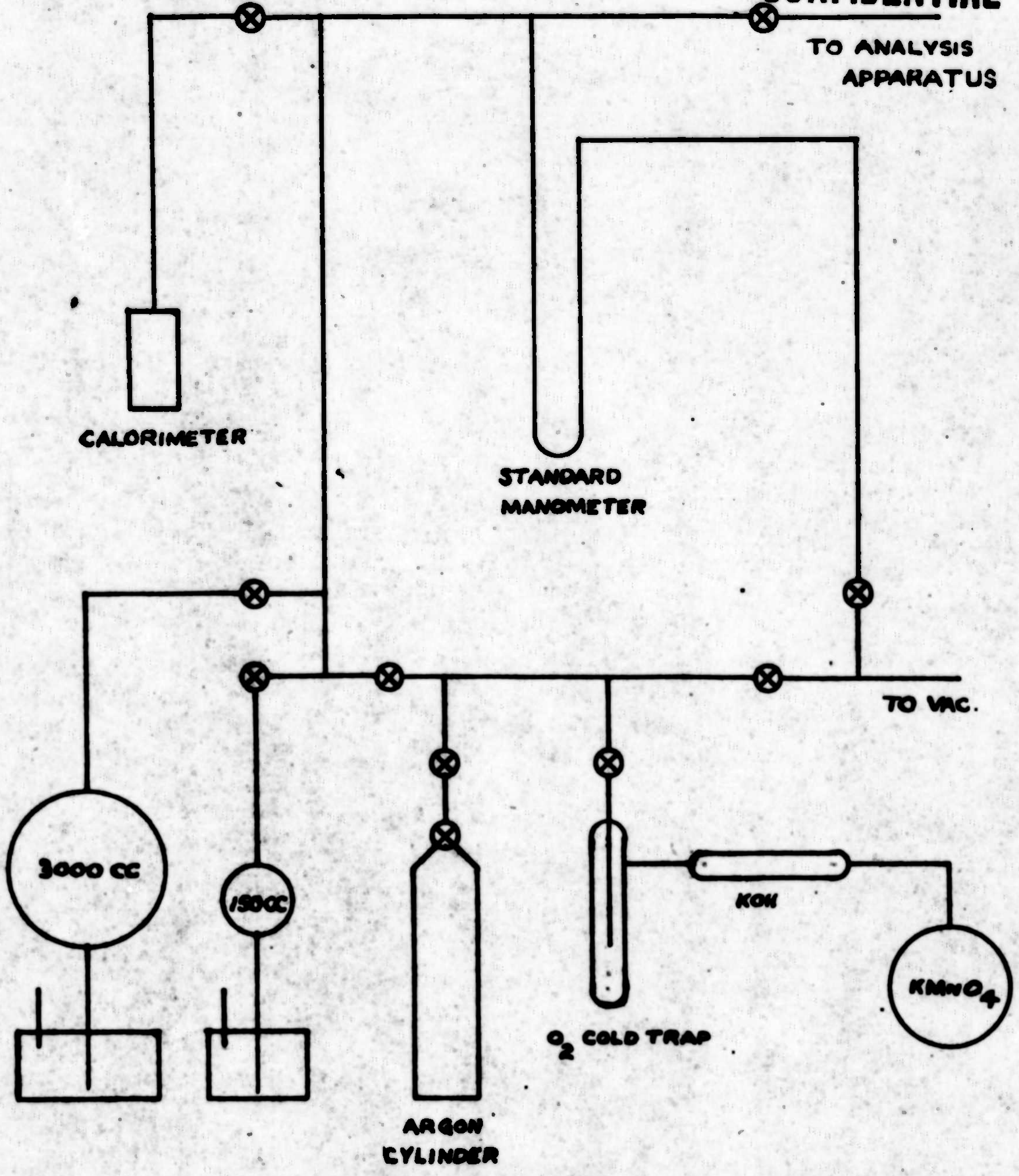

LINES FOR EQUILIBRIUM MEASUREMENTS
ON THE SYSTEM OXYGEN-ARGON

FIGURE 8

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CRYOGENIC LABORATORY
THE PENNSYLVANIA STATE COLLEGE

G.W.M
1/6/43

Both the three liter and the 0.2 liter calibrated bulbs could be filled with mercury from the reservoirs beneath them without contamination. By means of a bicycle pump or a vacuum pump, pressure or vacuum could be applied or the reservoirs and the mercury raised or lowered at will. The temperature of the lines was determined by five 0.1° thermometers placed at various parts of the system. Evacuation to a pressure of 10^{-6} mm. supplied the criterion of the tightness of the complete system.

Oxygen and Argon:

Pure oxygen was obtained by the method of Von Siemens[10] , Baker's "C.P." $KMnO_4$ was used. The permanganate bulb was first evacuated, then repumped after heating. The oxygen passed through a KOH drying tube and a glass wool filter and was finally collected in a liquid air cold trap, the fore run being discarded. From the cold trap, the liquid oxygen was distilled into the three liter measuring bulb and ultimately into the calorimeter. By analysis, oxygen prepared in this way had at the most an impurity of 0.01 per cent.

Pure argon was obtained from the Linde Air Products Company. They reported that the gas had been freed of last traces of oxygen and nitrogen chemically and that spectroscopic analysis indicated no trace of any other element except argon. Measurements taken in the high argon content region confirmed the absence of oxygen. The argon was taken from five liter cylinders, originally at 100 p.s.i., equipped with two valves and connected to the glass system by a copper seal. The pressure in the cylinders was never allowed to go down to atmospheric pressure. A vacuum of 10^{-5} mm. could be pumped on the complete line up to the valve nearest the cylinder. In this way, any possibility of contamination was avoided.

Procedure:

A sample of oxygen was measured volumetrically in either bulb. The weight of sample was calculated from the pressure, volume and temperature. This gas was then condensed into the calorimeter system which was kept at about 89°K. The amount of residual uncondensed oxygen was determined from another set of PVT data. The desired amount of argon was then likewise measured out and condensed. The mixture then stood at least twenty-four hours before any measurements were taken.

On Series I-VI vapor pressure measurements were taken between 550-850 int. mm. before taking any equilibrium data. Three to four points were taken at each composition after constant readings were attained in each case. The temperatures recorded were those read on gold resistance thermometer R-100. The composition of the liquid for these measurements is determined by subtracting respectively from the number of moles of each constituent originally condensed in the calorimeter as described above, the number of moles of each constituent in the small amount of gas in equilibrium with this mixture. Since, usually about 0.2 moles were condensed into the calorimeter and since approximately only 0.006 moles of gas were in equilibrium with this liquid, no appreciable error could be made in applying this correction.

The equilibrium data were obtained in the following manner. The mercury in the calibrated bulb to be used was caused to fall slowly, vaporizing material at constant pressure from the calorimeter. To produce slow vaporization the pressure on the reservoir was allowed to leak out slowly while at the same time supplying heat electrically to the calorimeter to keep the vapor pressure constant. By this means the pressure was kept constant within 5 mm. while vaporizing. This process took at least 45 minutes, and usually about 1-1/4 hours. The system was then thermally isolated for from 18 - 24 hours, (in which time the equilibrium pressure varied at the most about 10 mm. corresponding to a change in temperature of 0.2°C.), after which accurate temperature and pressure readings were taken. Finally, the calorimeter was shut off from the calibrated bulb. The quantity of material vaporized was then determined from its temperature, pressure and volume, after which the composition of this gaseous mixture was found by analysis. All equilibrium measurements were taken at approximately 760 int. mm. of mercury.

After the first gaseous sample had been analyzed, the calibrated bulb was evacuated to 10^{-6} mm., the calorimeter stopcock opened and a new sample vaporized. The same procedure was then applied to this second sample. Three or four vaporizations of approximately 0.02 to 0.03 moles of gas were made in this way. Finally the remaining material in the calorimeter was completely vaporized, the molar quantity of gas and its composition completing the data on one sample.

In the above procedure, if -

n_1 = moles of argon originally in the calorimeter system.

n_2 = moles of oxygen in the calorimeter system.

y_1 = moles of argon gas vaporized from the calorimeter system.

y_2 = moles of oxygen gas vaporized from the calorimeter system.

y_1^1 = moles of argon gas remaining in the calorimeter system.

y_2^1 = moles of oxygen gas remaining in the calorimeter system.

x_1 = moles of argon liquid remaining in the calorimeter system.

x_2 = moles of oxygen liquid remaining in the calorimeter system.

(where, by calorimeter system, we mean the calorimeter and filling line up to the calorimeter stopcock), then

$$x_1 = n_1 - (y_1 + y_1^1) \quad \text{. . . . .} \quad (18)$$

$$x_2 = n_2 - (y_2 + y_2^1) \quad \text{. . . . .} \quad (19)$$

For the first vaporization, the quantities n_1 and n_2 are the moles of argon and oxygen originally present in the calorimeter system. The quantities y_1 and y_2 are determined from the amount of material vaporized and its analysis. The quantity y_1^1 is calculated from:

$$y_1^1 = \left(\frac{y_1}{(y_1 + y_2)}\right) \frac{P \sum v/T}{R} \; \ldots\ldots\ldots\ldots \quad (20)$$

where the term in parenthesis represents the mole fraction of argon in the vapor, P represents the equilibrium pressure, $\sum v/T$ the sum of each gas volume in the calorimeter system divided by its absolute temperature, and R the gas constant. An equation similar to (20) exists for y_2^1.

For the next vaporization, the moles of argon and oxygen originally in the calorimeter system are $(x_1 + y_1^1)$ and $(x_2 + y_2^1)$ respectively. The other required quantities are determined analogously to the above.

Analysis:

The composition of all gaseous mixtures was ascertained by chemical analysis for oxygen. For analyses between 97 percent and 100 percent O_2, the method used was that of Badger[11] using copper with $NH_4Cl + NH_4OH$ as absorbent. The burette used for this work was calibrated with mercury. Readings could be made to 0.01 percent, but drainage errors limit the accuracy to about 0.015 percent. Analysis of the pure oxygen produced from $KMnO_4$ gave estimated results of 99.99 percent, 99.99 percent and 100.01 percent for three analyses.

For analysis of mixtures containing from 0-97 percent oxygen, a conventional Orsat procedure was employed using the commercial absorbent $SEEZO_2$(a). This absorbent was the most rapid and accurate absorbent of those tried; it behaved very similarly to Fieser's solution[12]. A three foot water jacketed burette was used for these analyses. Readings on this burette could be estimated to 0.03 percent but the accuracy of determination is probably from 0.05 to 0.10 percent. In these analyses, the apparatus was checked before each series by analysis of O_2 in air.

(a) Furnished by the Hays Corporation, Michigan City, Indiana

The method of transfer of the gas to be analyzed to the burette involved no intermediate containing vessels. The sample was drawn into the burette, thru a system which had previously been evacuated to 10^{-5} mm. pressure.

After Series I, all analyses were taken in duplicate.

Data:

It was noticed that the first vaporization of each series gave a vapor which was not in accord with the results of succeeding vaporizations. This first measurement was always high in argon content. With the method used of filling the calorimeter, the gas phase originally consisted of 100 percent argon. It is demonstrated presently that the time to reach equilibrium for this is too long to be practical(a) Therefore, the results of this first vaporization were discarded in all series.

It will be shown presently that the rates of gas diffusion, evaporation and condensation were rapid enough to establish equilibrium in all other cases.

The term known least accurately is the term y^1 of equation (20). This term could be exactly calculated if the temperatures of all parts of the calorimeter system from the calorimeter, which was at about 90°K., to the exterior lines, which were at about 300°K., were known. The temperature distribution in the gradient could only be approximated. Consequently, in the final vaporization, on account of the small amount of liquid left in the calorimeter, an appreciable error might be made. Arbitrarily, if y^1/x was greater than 0.2, the result of the vaporization was discarded. All other results are included in Table VIII.

Vapor Pressures:

The total pressure above mixtures from 0 - 87 percent argon was measured as described above. The values are given in Table IV. The observed pressure in international millimeters and temperature in degrees Kelvin are given in columns two and three respectively, for liquids of the compositions given in column one. For a given composition the results of Table IV indicate that the

---

(a) Only one vapor produced from the first vaporization ever reached complete equilibrium. After 72 hours analysis showed the mixture to be at equilibrium. This data was used in a later calculation as will be seen.

Table IV

VAPOR PRESSURE OF ARGON-OXYGEN MIXTURES EXPERIMENTAL DATA

Mole Per Cent Argon in Liquid	P int. mm.	T. deg. Kelvin*	Δ P (obs.-calc.)	Δ T (calc.-obs.)
0	554.93	87.303	- 0.3	- 0.006
0	649.19	88.722	+ 0.1	+ 0.002
0	761.08	90.211	+ 0.4	+ 0.004
0	801.21	90.714	- 0.3	- 0.002
0.39	743.74	89.974	+ 0.2	+ 0.002
0.41	751.32	90.075	- 0.3	- 0.004
0.47	747.61	90.020	+ 0.3	+ 0.003
0.48	721.49	89.681	+ 0.2	+ 0.002
0.73	751.07	90.051	0	0
0.84	735.69	89.845	+ 0.2	+ 0.002
1.54	765.57	90.195	- 0.4	+ 0.004
1.64	774.98	90.306	- 0.4	+ 0.004
2.44	759.08	90.102	- 3.0	- 0.040
2.57	774.27	90.293	- 3.9	- 0.051
3.08	757.65	90.055	- 3.5	- 0.052
3.15	848.67	91.165	- 5.4	- 0.060
3.15	751.51	89.993	- 5.0	- 0.067
3.16	643.55	88.542	- 4.7	- 0.069
3.18	546.30	87.054	- 4.0	- 0.069

* As read on R-100.

Table IV (continued)

VAPOR PRESSURE OF ARGON-OXYGEN MIXTURES EXPERIMENTAL DATA

Mole Per cent Argon in Liquid	P int. mm.	T deg. Kelvin	Δ P (obs.-calc.)	Δ T (calc.-obs.)
6.41	775.08	90.093	- 2.6	- 0.030
7.73	764.17	89.867	+ 1.1	+ 0.014
7.86	762.36	89.832	0	0
8.03	845.43	90.824	+ 0.3	+ 0.002
8.04	757.01	89.760	+ 0.3	+ 0.003
8.07	641.44	88.205	+ 0.4	+ 0.004
8.08	546.34	86.761	- 1.1	- 0.020
14.1	760.80	89.512	+ 0.1	+ 0.002
14.2	766.62	89.541	+ 2.9	+ 0.036
15.2	771.55	89.569	+ 2.6	+ 0.034
15.76	762.52	89.452	+ 0.3	+ 0.004
15.80	649.34	87.935	+ 0.8	+ 0.011
15.83	550.01	86.430	+ 0.6	+ 0.011
25.4	751.10	88.876	+ 0.9	+ 0.011
26.3	745.07	88.759	+ 1.4	+ 0.017
28.36	823.64	89.659	- 0.2	- 0.002
28.40	761.14	88.892	+ 0.3	+ 0.004
28.44	710.22	88.245	- 0.3	- 0.003
28.49	631.88	87.160	- 0.4	- 0.006

Table IV (continued)

VAPOR PRESSURE OF ARGON-OXYGEN MISTURES EXPERIMENTAL DATA

Mole Per cent Argon in Liquid	P int. mm.	T deg. Kelvin	Δ P (obs.-calc.)	Δ T (calc.-obs.)
65.2	753.97	87.768	- 0.8	- 0.010
67.6	750.28	87.667	- 0.3	- 0.005
68.3	738.12	87.507	- 1.2	- 0.015
68.7	735.30	87.445	+ 0.3	+ 0.005
69.69	852.45	88.826	+ 1.9	+ 0.021
69.83	785.47	88.033	+ 1.5	+ 0.017
69.87	688.67	86.796	+ 1.2	+ 0.015
86.65	746.31	87.302	+ 1.1	+ 0.013
86.92	786.97	87.805	+ 0.5	+ 0.004
87.16	768.33	87.564	+ 1.1	+ 0.013

relationship

$$\log_{10} P = -A/T + B$$

is followed very closely in the pressure range studied. Thus the data can be represented as in Table V, where column one gives the composition in mole percent argon in the liquid phase, and columns two and three give respectively the corresponding constants A and B for this composition. The fit of these equations with the experimental data is shown in columns four and five of Table IV. It is seen that the mean deviation is 0.7 mm., corresponding to a temperature deviation of 0.009°C. Thus, at these pressures the accuracy of temperature measurements is the determining factor in the measurement. The data have been extrapolated to the normal boiling point of pure argon to give a value of 87.23 ± .05°K. (-185.93°C.). Values for the normal boiling point of argon reported in the literature are those of Ramsay and Travers (-186.1°C.)[13], Crommelin (-185.84°C.)[14], Mathias, Onnes and Crommelin (-185.66°C.)[15] and Bourbo and Ishkin (-185.9°C.)[16]. The value which we find for the normal boiling point of oxygen, 90.20 ± .02°K. (-182.96°C.) is in perfect agreement with the value of Hoge and Brickwedde[17], viz. 90.19 based upon a critical study of the literature.

Table VI gives values of the temperature in degrees Kelvin at which a total pressure of 760 int. mm. of mercury is reached, for various mixtures. These values, calculated from the data of Table V represent the boiling curve at this pressure. Likewise calculated from the data of Table V, Table VII lists the total pressure for various mixtures at a temperature of 88.57°K.

Equilibrium Data:

Table VIII lists the experimentally obtained equilibrium data. Although the pressures differed slightly from one atmosphere, the effect of this small difference on the vapor composition is negligible. Accordingly, a plot was made of y/x versus x representing this data and a smooth curve drawn through the results. Figure 9 shows this plot on a smaller scale. For convenience the

TABLE V

THE VAPOR PRESSURE OF ARGON-OXYGEN MIXTURES

$$\log_{10} P = -A/T + B$$

Mole Per cent Argon in Liquid	A	B
0	370.20	6.9849
1	369.68	6.9816
2	369.20	6.9786
3	368.74	6.9759
4	368.30	6.9734
5	367.88	6.9710
10	365.83	6.9594
15	364.00	6.9497
20	362.37	6.9419
25	360.92	6.9354
30	359.63	6.9298
40	357.27	6.9196
50	355.27	6.9102
60	353.56	6.9013
70	352.07	6.8937
80	350.70	6.8852
90	349.39	6.8768
100	348.12	6.8685

TABLE VI

BOILING POINT OF ARGON-OXYGEN MIXTURES AT 760 INT. MM. TOTAL PRESSURE

Mole Per cent Argon in Liquid	Boiling Point Degrees Kelvin
0	90.202
1	90.148
2	90.097
3	90.044
4	89.992
5	89.941
10	89.695
15	89.459
20	89.230
25	89.015
30	88.819
40	88.459
50	88.169
60	87.939
70	87.735
80	87.579
90	87.435
100	87.298

Table VII

TOTAL PRESSURE ABOVE ARGON-OXYGEN MIXTURES

AT 88.57°K.

Mole Per cent Argon in Liquid	Total Pressure 88.5°K. (int. mm.)
0	636.3
2	645.5
10	674.2
20	708.6
30	740.0
40	768.6
50	792.2
60	811.3
70	828.7
80	842.2
90	854.7
100	866.8

Table III

EQUILIBRIUM DATA FOR THE SYSTEM ARGON-OXYGEN

x Mole Per cent of argon in liquid	y Mole Per cent of argon in vapor	P Total Pressure	K (y/x)
2.44	3.65	759.1	1.49
1.64	2.40	775.0	1.47
12.09	17.30	760.8	1.431
11.02	15.89	750.2	1.442
26.69	35.78	745.1	1.341
66.66	71.02	750.3	1.065
67.69	71.45	738.1	1.056
0.87	1.30	735.7	1.49
0.73	1.09	751.1	1.49
0.48	0.72	721.5	1.50
0.41	0.60	751.3	1.47
0.39	0.59	743.7	1.51
86.21	87.59	746.0	1.016
86.61	88.01	746.3	1.016
86.96	88.28	787.0	1.015
43.84	52.62	765.0	1.200
41.18	50.22	771.4	1.219

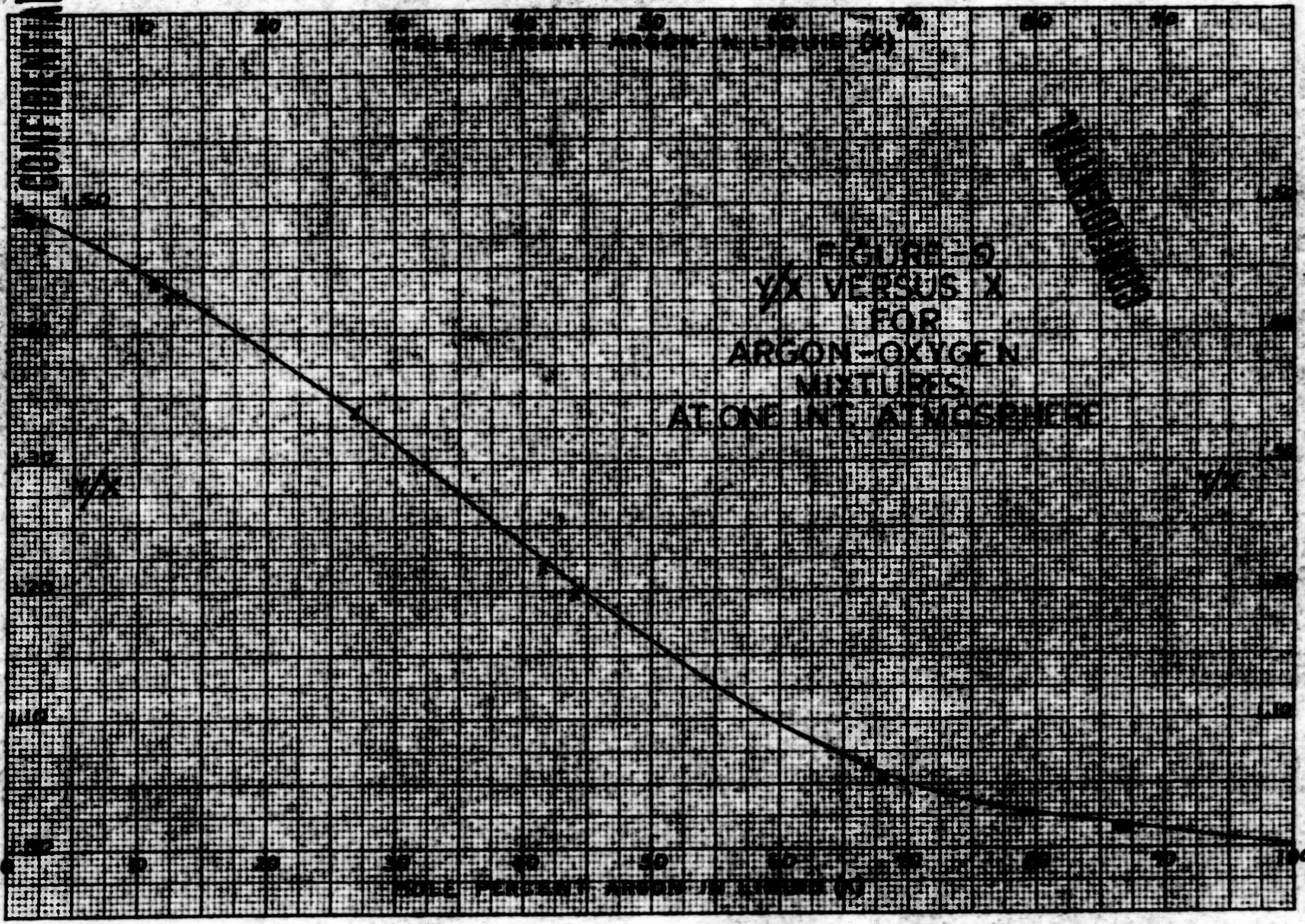

FIGURE 9
Y/X VERSUS X
FOR
ARGON-OXYGEN
MIXTURES
AT ONE INT. ATMOSPHERE

smoothed values of y/x are listed in Table IX.

The accuracy of these results is determined by the accuracy of analysis. Since each point depends on either two or three analyses, the values of the mole percent of gas in equilibrium with liquid of a specific concentration may be in error by 0.03 mole percent for low argon concentrations and by 0.15 mole percent for high argon concentrations. The third column of Table IX lists the percentage error in y/x on this basis.

The conventionally represented T, X diagram, summarizing all the data is shown in Figure 10. The low volatility of argon at high concentrations found by Schilling and by Bourbo and Ishkin has been substantiated. Figure 11 is a more detailed plot of argon-oxygen liquid-vapor equilibria at very low argon concentrations, the region of interest for calculations involving an oxygen tower.

Equilibrium Data at 88.57°K.

Since the calorimetric apparatus could be used at pressures only slightly above one atmosphere, the effect of pressures on the equilibrium values could not be found. Likewise, exact values for the equilibrium data represented isothermally were not obtained. However, if a temperature was chosen in the mean range of of the results at one atmosphere, an isothermal representation of the data could be obtained to a good approximation. The temperature chosen was 88.57°K.

The partial pressure of argon in the gas, P_1, may be related to the vapor pressure of the pure liquid by the equation -

$$P_1 = P_1^o \; a_1 \; \ldots\ldots\ldots\ldots\ldots \quad (21)$$

where a_1 is the activity of argon in the solution. If the activity coefficient be assumed coustant for the small temperature interval between the temperature corresponding to a total pressure of 760 mm. and 88.57°K., then -

$$P_1 \; (88.57°K.) = P_1 \; (T) \frac{P_1^o \; (88.57°K.)}{P_1^o \; (T)} \; \ldots\ldots\ldots\ldots \quad (22)$$

Table IX

SMOOTHED VALUES OF EQUILIBRIUM DATA FOR THE SYSTEM ARGON-OXYGEN AT ONE INT. ATM.

Mole Per cent Argon in Liquid (x)	K (y/x)	Estimated % Accuracy in K.
0	1.50	---
1	1.495	3.0
2	1.489	1.5
10	1.446	1.5
20	1.384	0.7
30	1.310	0.5
40	1.226	0.4
50	1.151	0.3
60	1.094	0.3
70	1.057	0.2
80	1.031	0.2
90	1.014	0.2
100	1.000	

17 b

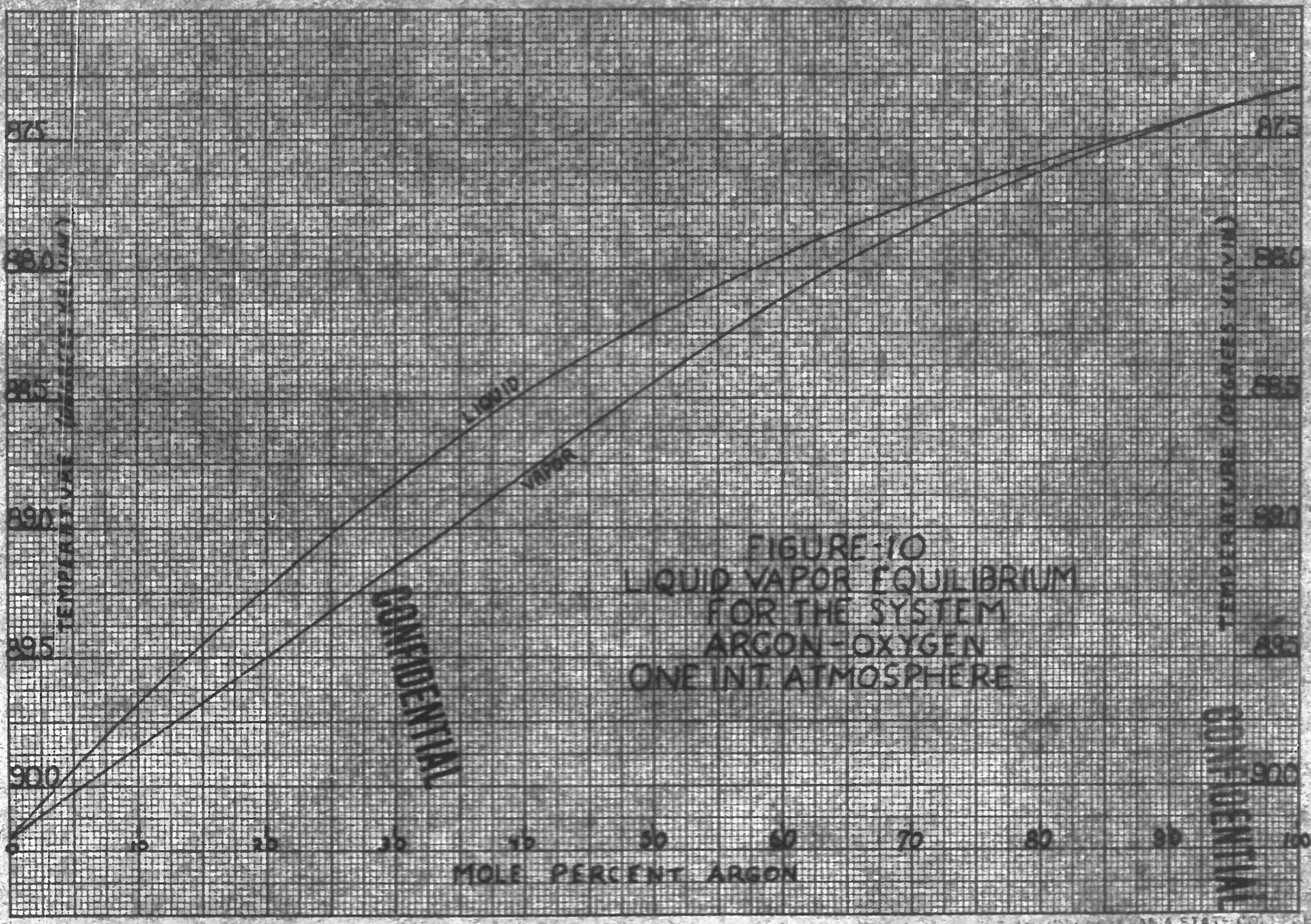

FIGURE 10
LIQUID VAPOR EQUILIBRIUM
FOR THE SYSTEM
ARGON - OXYGEN
ONE INT. ATMOSPHERE

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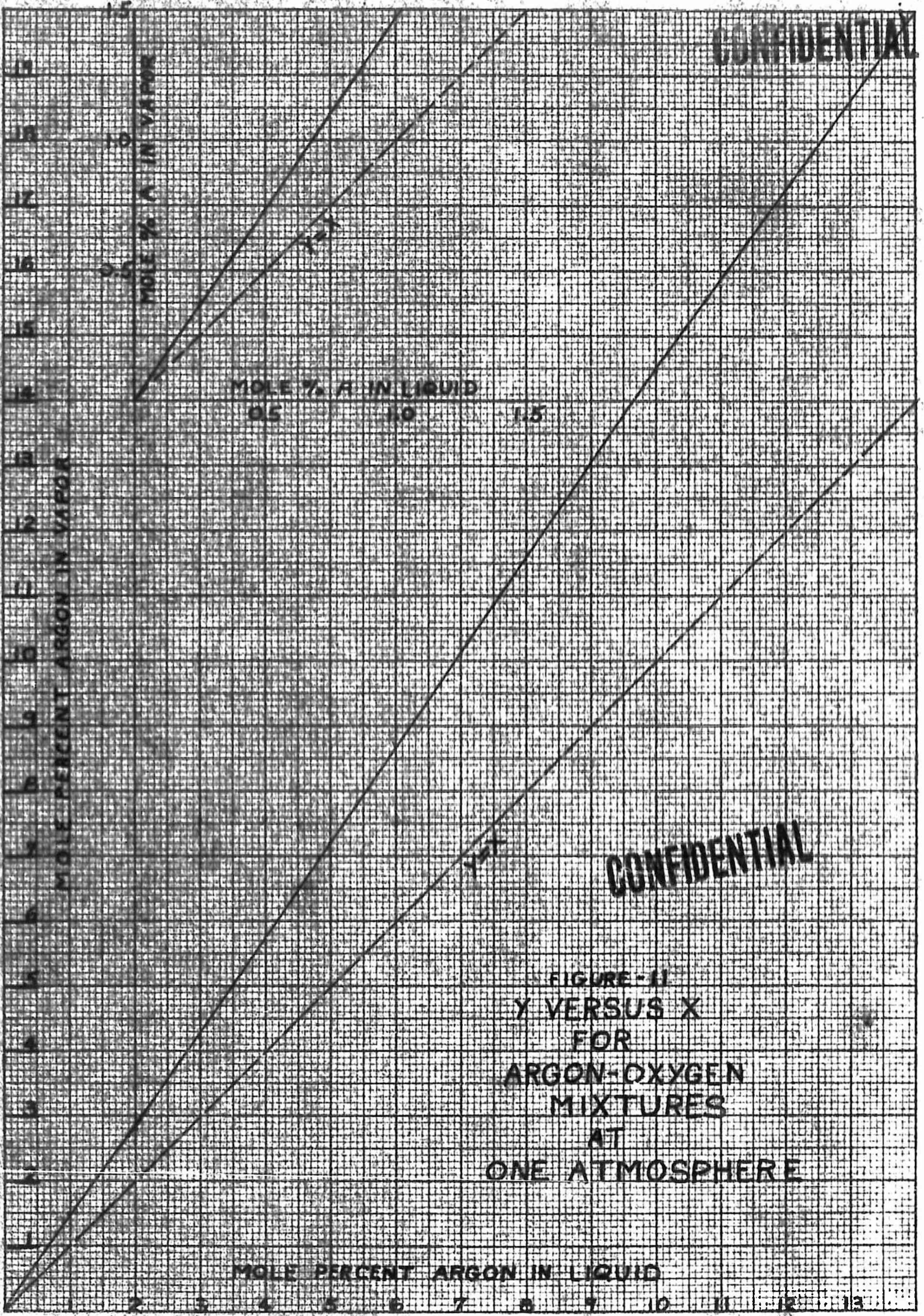

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FIGURE-11
Y VERSUS X
FOR
ARGON-OXYGEN
MIXTURES
AT
ONE ATMOSPHERE

where P_1 (88.57°K.) is the partial pressure of argon at 88.57°K.

P_1 (T) is the partial pressure of argon at T.

P_1^o (88.57°K.) is the vapor pressure of pure liquid argon at 88.57°K.

P_1^o (T) is the vapor pressure of pure liquid argon at T.

T is the temperature corresponding to an equilibrium pressure 760 mm.

Likewise, the similar equation -

$$P_2\,(88.57^\circ K.) = P_2\,(T)\,\frac{P_2^o\,(88.57^\circ K.)}{P_2^o\,(T)} \quad \ldots\ldots\ldots\ldots\ldots \quad (23)$$

relates the partial pressure of oxygen at 88.57 to the partial pressures experimentally obtained at 769 mm.[a]. Table X summarizes the results over the complete concentration range. It is seen that the results obtained at 88.57°K. differ from thos obtained at 760 int. mm. by only 0.9 per cent at the greatest. Figure 12 is a plot of y/x against x for a temperature of 88.57°K. The P, X diagram at 88.57°K. is shown in Figure 13. In figure 14 the partial pressures of argon and oxygen are plotted against the mole fraction of argon in the liquid at 88.57°K. It is seen that very appreciable differences from Raoult's law exist.

(a) An equation similar to (22), which however allows for the change in the activity of the pure components with temperature is:

$$P_1\,(88.57^\circ K.) = P_1\,(T)\,\frac{\left[P_1(88.57^\circ K.)+P_2(88.57^\circ K.)\right]\left[P_1^o(88.57^\circ K.)\right]\left[N_1P_1^o(T)+N_2P_2^o(T)\right]}{\left[P_1(T)+P_2(T)\right]\left[N_1P_1^o(88.57^\circ K.)+N_2P_2^o(88.57^\circ K.)\right]\left[P_1^o(T)\right]} \quad \ldots\ldots \quad (24)$$

and gives results almost identical with equation (22). The use of equation (24) is equivalent to obtaining the partial pressure at 88.57°K. from that experimentally determined at T, by multiplying the latter by P_1 (Raoults, 88.57°K.)/P_1 (Raoults,T), i.e. by the ratio of the partial pressures calculated from Raoult's law at the two temperatures.

Table X

EQUILIBRIUM IN SYSTEM ARGON-OXYGEN AT 88.57°K.

Mole Percent A in Liquid	Mole Percent A in Vapor 760 mm.	Mole Percent A in Vapor 88.57°K.
0	0	0
1	1.495	1.509
2	2.978	3.006
10	14.46	14.55
20	27.68	27.77
30	39.30	39.33
40	49.04	49.02
50	57.55	57.49
60	65.64	65.55
70	73.99	73.89
80	82.48	82.40
90	91.26	91.21
100	100.00	100.00

14

18-b

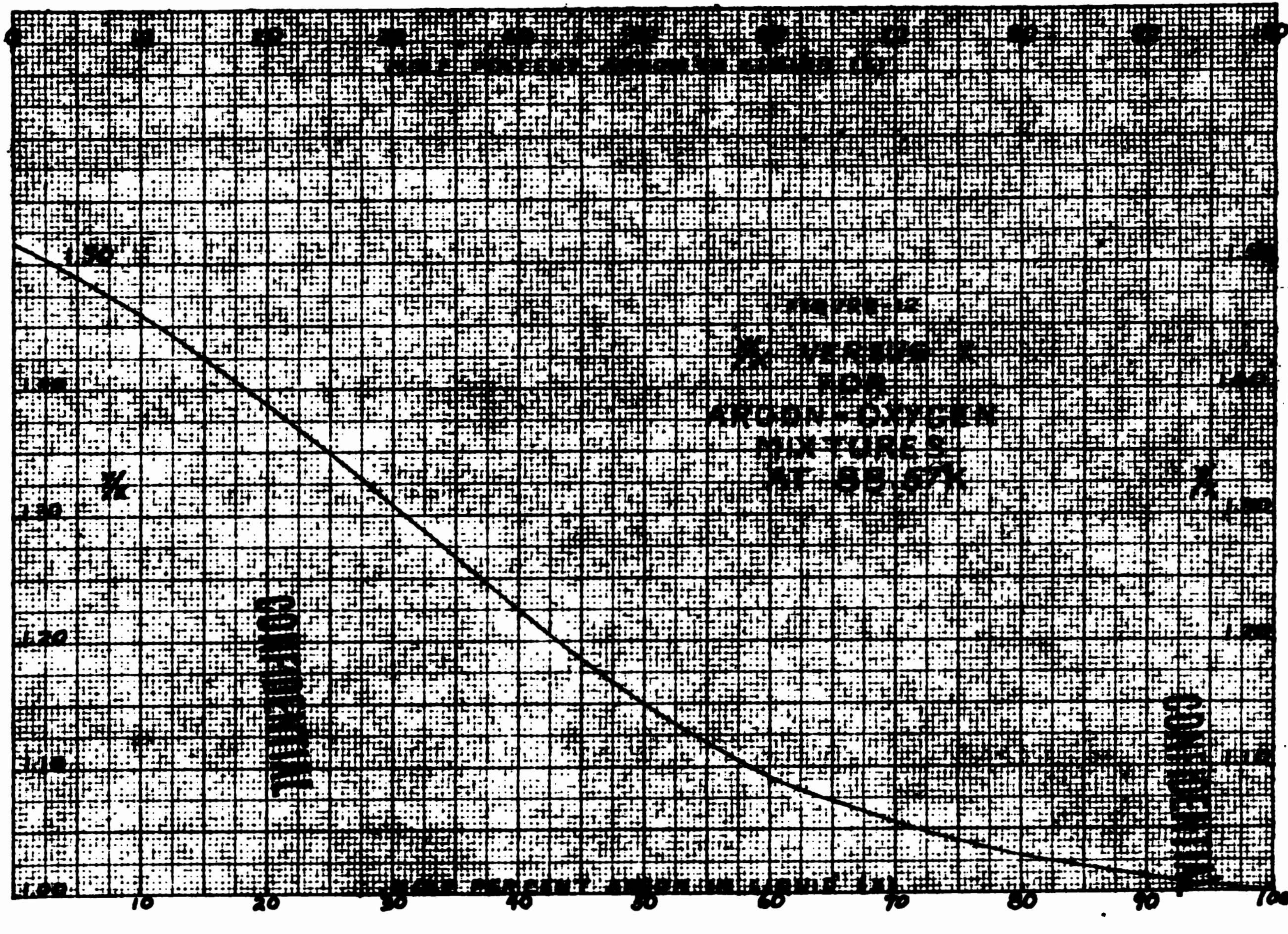

FIGURE 12
% VERSUS X
FOR
ARGON - OXYGEN
MIXTURES
AT 89.5°K

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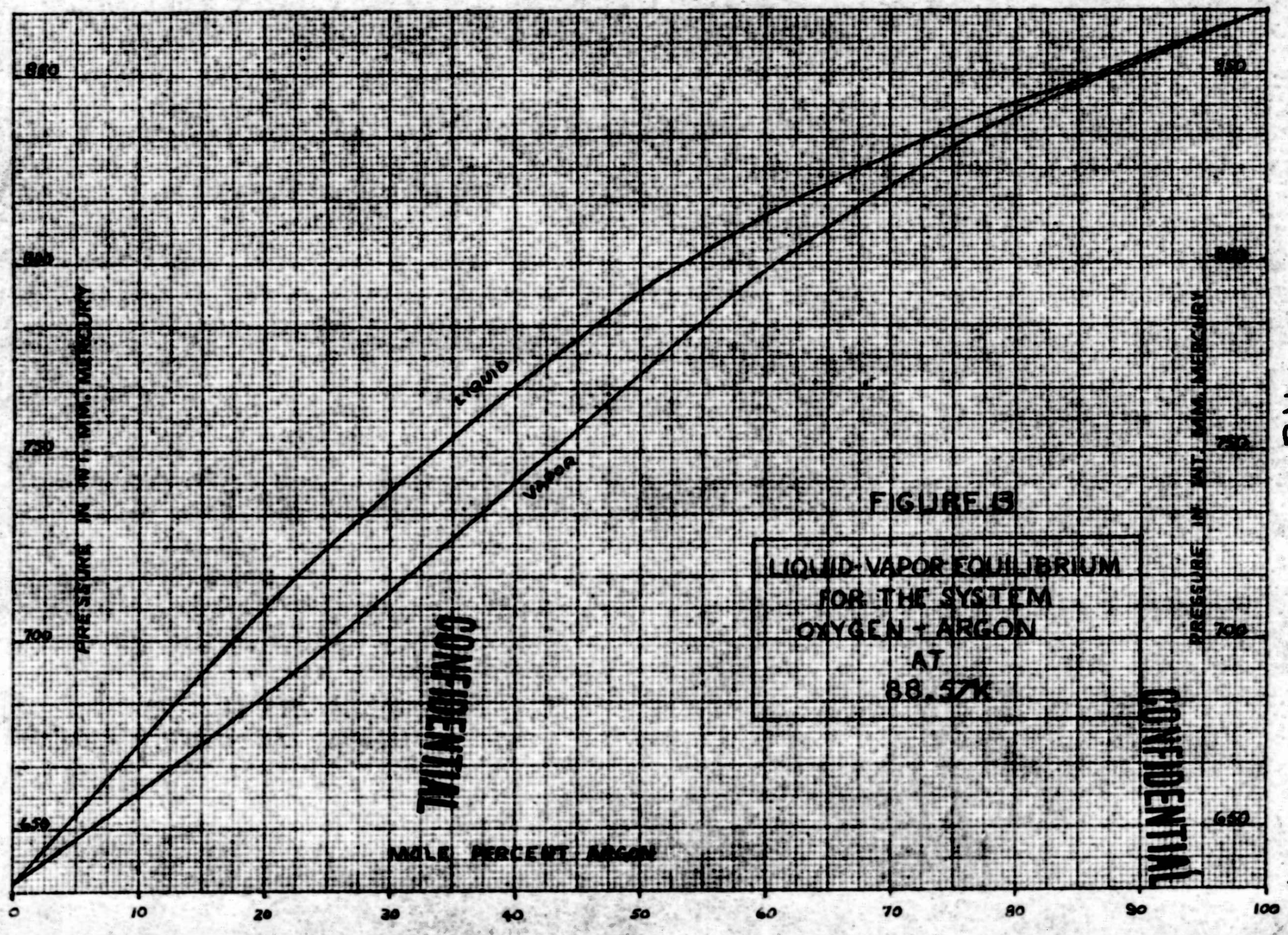

FIGURE 13

LIQUID-VAPOR EQUILIBRIUM
FOR THE SYSTEM
OXYGEN + ARGON
AT
88.57K

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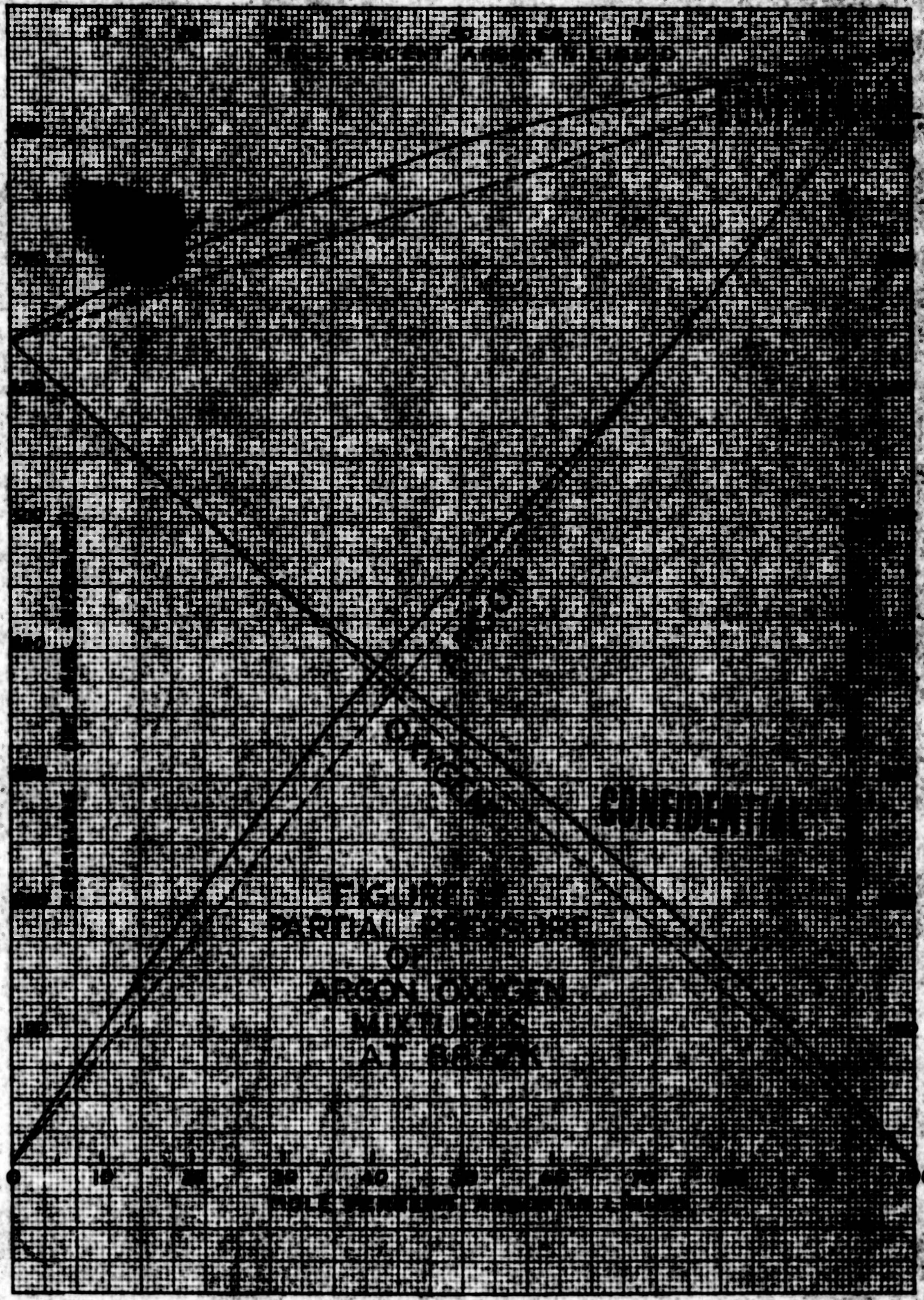

FIGURE [illegible]
PARTIAL PRESSURE
OF
ARGON OXYGEN
MIXTURES
AT [illegible]°K

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In Table XI the data of this research are compared with that of Bourbo and Ishkin, and that of Schilling. Although the data of the latter are given at different temperatures, and at different pressures from this research, correlations can be made. The check of the experimental values with the data of Bourbo and Ishkin is excellent from 0 - 40 per cent, but is not as good at higher argon concentrations. The work of Schilling, done according to the author to "engineering accuracy" agrees with the data found in this work within his probable experimental error at all except the middle concentration range.

The data of this research can be proved free of appreciable error due to lack of equilibrium.

The reversible transfer of argon from the gas to the liquid phase is represented by

$$A_l \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A_g \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (25)$$

where A_l represents the mole fraction of argon in the liquid phase, A_g in the gas phase and k_1 and k_2 are the specific reaction constants for the reactions as written. Then -

$$\frac{d\,A_g}{dt} = k_1\,A_l - k_2\,A_g \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (26)$$

where the derivative expresses the change in concentration (expressed as mole fraction at constant total pressure) of argon in the gas with time. Thus at equilibrium

$$k_2\,A_g = k_1\,A_l \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (27)$$

or

$$\frac{A_g}{A_l} = \frac{k_1}{k_2} = K \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (28)$$

where K is the volatility constant (y/x). The equation representing the material balance in the system is

Table XI

EQUILIBRIUM IN SYSTEM ARGON-OXYGEN

Mole Per cent Argon in Liquid (x)	Mole Per cent Argon in Vapor (y) (This Research) 88.57°K.	y Schilling 760 mm.	y B & I 87 °K.	y B & I 90 °K.
0	0	0	0	0
1	1.509	1.55	1.51	---*
10	14.55	14.46	14.5	14.6
20	27.77	26.90	27.7	27.9
30	39.33	37.90	39.2	39.4
40	49.02	47.78	49.2	48.8
50	57.49	57.00	58.0	57.8
60	65.55	65.72	66.7	66.2
70	73.89	74.20	74.9	74.5
80	82.40	82.50	83.3	82.9
90	91.21	91.10	91.4	91.4
100	100.00	100.00	100.00	100.00

* Value uncertain from numerical data given in publication.

$$n_g A_g + n_l A_l = n_A \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (29)$$

where

n_g = the total moles of gas

n_l = the total moles of liquid

n_A = the total moles of argon

Substituting (28) and (29) in (26)

$$\frac{d A_g}{\frac{K n_A}{n_l} - A_g\left(\frac{K n_g}{n_l} + 1\right)} = k_2 \, dt \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (30)$$

Integrating, and including the initial condition ($t = 0$; $A_g = A_g^o$)

$$\frac{1}{\left(\frac{K n_g}{n_l} + 1\right)} \log \frac{\left[\frac{K n_A}{n_l} - A_g^o \left(\frac{K n_g}{n_l} + 1\right)\right]}{\left[\frac{K n_A}{n_l} - A_g \left(\frac{K n_g}{n_l} + 1\right)\right]} = K_2 t \quad . \ (31)$$

The constant k_2 can be solved for using data obtained in the first vaporization of each series. It has been stated that due to the method of filling the calorimeter, the vapor originally consisted of 100 mole per cent argon, and in the time of standing allowed, the vapor did not come into equilibrium with the liquid. Since analyses of the vapor were measured after 18 - 24 hours standing, data are available to solve for the constant k_2 in equation (31). The initial concentration of argon, A_g^o, was calculated by assuming that the vapor formed was in equilibrium with the "average liquid" in the calorimeter during vaporization and allowing for the number of moles of pure argon originally in the lines. The value obtained for k_2 was 0.027 hours^{-1}. Using this value of k_2, the percentage error due to asymptotic approach to equilibrium in any vaporization can be calculated, however, a more accurate value of k_2 to be discussed presently, was used. The computed errors are listed in Table XII as a function of the concentration of argon in the liquid. It is seen that the maximum error produced in the measurements due to poor equilibrium is 0.3 per cent. The data and calculated values of k_2 are summarized in Table XIII.

To determine k_2 more accurately the calorimeter was filled with three-fourths of a mole of liquid oxygen while the large bulb and connecting lines were filled with gaseous argon at atmospheric pressure. The calorimeter stopcock was then opened and at measured times analyses of the vapor was taken. The data at the several time intervals together with the values of k_2 derived therefrom are summarized in Table XIV. In these measurements the volume of vapor taken was about five times that taken during the actual equilibrium measurements, therefore the rate constant corresponding to the latter should be approximately 0.05 hours^{-1} compared to the average value of 0.027 hours^{-1} found from the data in Table XIII. In view of the fact that the values in Table XIII were rather close to equilibrium the value of 0.05 hours^{-1} is the value chosen for k_2.

While determining k_2 more accurately it was possible at the same time to obtain a check point on the equilibrium system in which a very large amount of material was contained in the calorimeter. A summary of the data for this point appears below:

$T = 88.42^{\circ}K$
$P = 707.90$ mm.
Mol per cent O_2 in gas = 73.31
Mol per cent A in gas = 26.69
Mol per cent O_2 in liquid = 80.80
Mol per cent A in liquid = 19.20
$y/x = 1.390$
y/x from plot at $88.57^{\circ}K.$ = 1.395

This value of 1.390 for the equilibrium constant at $88.42^{\circ}K.$ corrected to $88.57^{\circ}K.$ is 1.398.

Table XII

ERROR IN K (y/x) PRODUCED BY CHOSEN EQUILIBRIUM TIME OF 18-24 HOURS

Mole Per cent Argon in Liquid	Percent Error in K
1	0.24
10	0.18
20	0.12
30	0.09
40	0.06
50	0.04
60	0.03
70	0.02
80	0.02
90	0.02

Table XIII

CALCULATION OF k_2 FROM EQUILIBRIUM MEASUREMENTS

Quantities utilized in Eq. (15)	Run 4	Run 6
K	1.437	1.061
N_g	0.03657	0.0258
N_e	0.23220	0.1418
N_a	0.04158	0.1171
A_g	0.2325	0.7600
A_g°	0.2570	0.8290
t_2	12	12
k_2	0.0258	0.0290

Table XIV

DATA FOR EXPERIMENTAL DETERMINATION OF k_2

Time in hours	% O_2	k_2 for full bulb	k_2 for volume used in equilibrium measurements
0	0	- - -	- - -
2	0	- - -	- - -
6	83	0.014	0.070
16 1/2	60	0.013	0.065
35 3/4	50	0.011	0.055

The accuracy of the data was tested using the Duhem equation as outlined in Part I of the report. The results of this calculation are given in Table XV.

TABLE XV

THIS RESEARCH A - O_2 ISOTHERM AT 88.57°K

N_1 (O_2)	$a_1 = f_1/f_1^o$	a_1 (plot)	Percent Dev.
0.99	0.9902	0.9900	+ 0.02
0.98	0.9805	0.9800	0.05
0.90	0.9006	0.8995	0.12
0.85	0.8491	0.8492	0
0.80	0.7986	0.7998	- 0.15
0.75	0.7493	0.7490	+ 0.04
0.70	0.6994	0.6987	0.10
0.60	0.6093	0.6091	0
0.50	0.5231	0.5231	0
0.40	0.4337	0.4326	+ 0.21
0.30	0.3354	0.3330	0.72
0.20	0.2296	0.2279	0.82

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VAPOR-LIQUID EQUILIBRIUM DATA ON THE SYSTEM OXYGEN-NITROGEN-ARGON

DETAILED DESCRIPTION OF THE NEW APPARATUS

Equilibrium Vessel and Cryostat

A detailed drawing of an improved equilibrium apparatus appears in Fig. 15. The apparatus itself is similar in general design to Isothermal Calorimeter "C". This design was used because of the ease with which it can be adjusted to any given temperature between 58° and 300°K. (using only liquid air as the cooling agent) and held there for great lengths of time with a minimum of adjustment.

The equilibrium vessel (A) was constructed of copper tube 1" O.D., 3/4" I.D., and 5" long. The bottom and top plugs were screwed into the tube to a depth of 1/4" giving an effective inside length of 4". A double thread groove was cut into the body of this cylinder and a bifilar wound constantan heater of 75 ohms resistance wrapped into the threaded grooves. After the heater had been painted with bakelite and baked for 4-8 hours, a covering of copper foil was soldered over it to cut down outward radiation of heat. Two thermocouples (B) and (B^1) are inserted into a 1/16" copper well soft soldered to the bottom of the equilibrium vessel.

The filling tube (C) was made from 5/16" German silver tubing with a wall thickness of 0.009". A heavy shield consisting of a cylindrical copper bottom (D) and a top of lead cast into a copper ring (E) surround the equilibrium vessel. Both the top and bottom of the shield are equipped with heaters. Thermocouples are placed on the bottom of the shield (F), top of the shield (G), filling tube just inside the top shield (H), filling tube just outside the shield top (I), and 2" above the shield top (J). The last three thermocouples are used to be sure that the tube is warmer than the equilibrium vessel and thus eliminate the possibility of refluxing.

The shields are hung from a copper ring (N) which is silver soldered to the top of the cryostat can (O). All leads (heaters and thermocouples) circle inside this copper ring where they are well paraffined to insure thermal contact with the ring.

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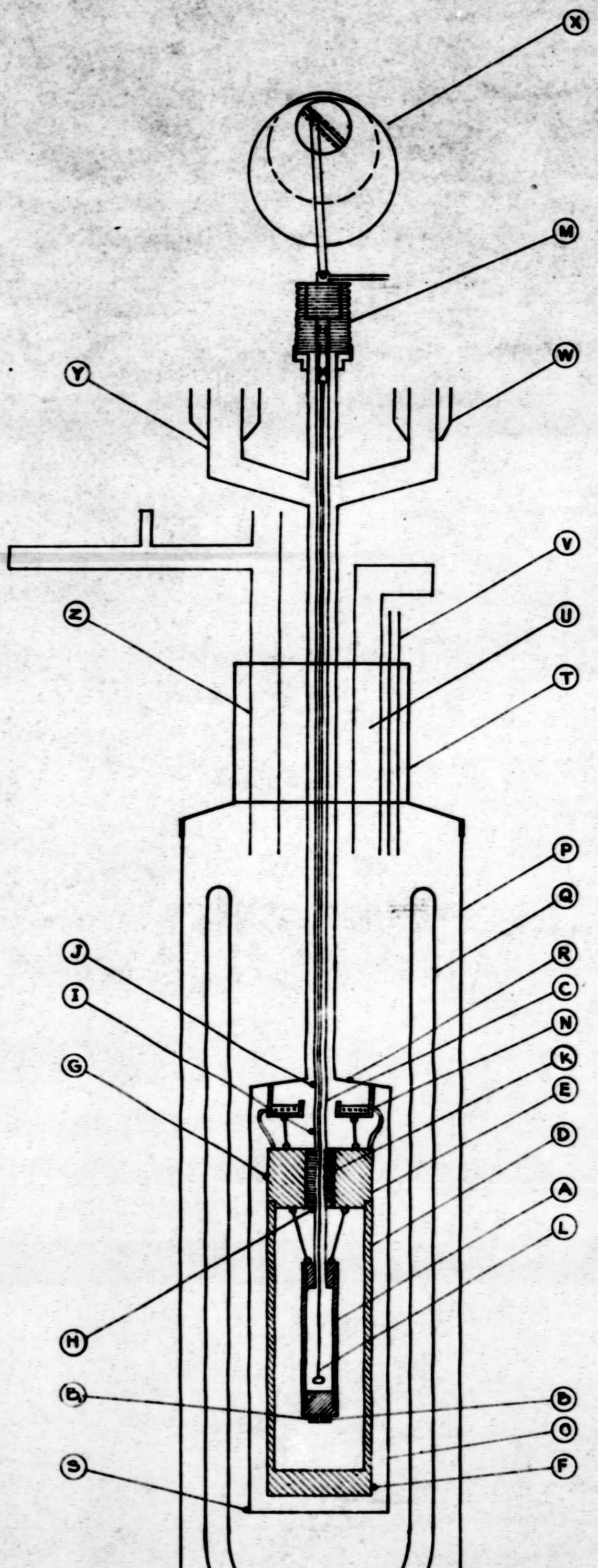

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EQUILIBRUM APPARATUS
AND CRYOSTAT
FIG [illegible]

A regenerator (K) is located in the filling tube at the point where it passes through the shield top. It consists of a tube 7/8" in diameter and 1-1/2" long with silver soldered connections to the filling tube at both ends. It is filled with small wire gauze discs which make intimate contact with the wall of the tube. This device ensures contact with the shield top of any gas passing up or down the filling tube, thus eliminating a large source of heat leak.

The stirrer (L) was mounted on a tube of 1/8" German silver tubing with a 0.009" wall thickness. Originally, 3 small discs were soldered at 1/2" intervals on the bottom of this tube for the stirring of the liquid. It was later discovered that these discs caused splashing of the liquid and the droplets thus formed were evaporated giving a vapor which was not in equilibrium with the liquid. The stirrer was modified by cutting away a large fraction of the cross section of the tube for a length of 6 inches. This section was flattened to ribbon 0.4 mm. wide and 0.2 mm. thick and a loop made in its end. This arrangement has made a very satisfactory stirrer.

The stirrer rod is fastened at top to a sylphon bellows (M); the bellows and attached stirrer are both moved by an adjustable eccentric driven by a Flexo Action gear and motor system which turns at the rate of sixty times a minute.

A schematic drawing of the cryostat with all external glass lines appears in figure 16. The mixture in the equilibrium vessel is vaporized through a very short connecting line into the 500 cc vaporization bulb shown in figure 16. This bulb is connected to a mercury reservoir whose pressure can be decreased automatically by means of a solenoid valve actuated by a mercury manometer with contacts connected to the main equilibrium system. Thus, as the vaporized liquid increases the pressure in the system, the manometer contact actuates the solenoid valve in the mercury reservoir system and releases pressure which allows the mercury to fall in the vaporization bulb, increasing the volume and decreasing the pressure in it. This action takes place very rapidly and the pressure

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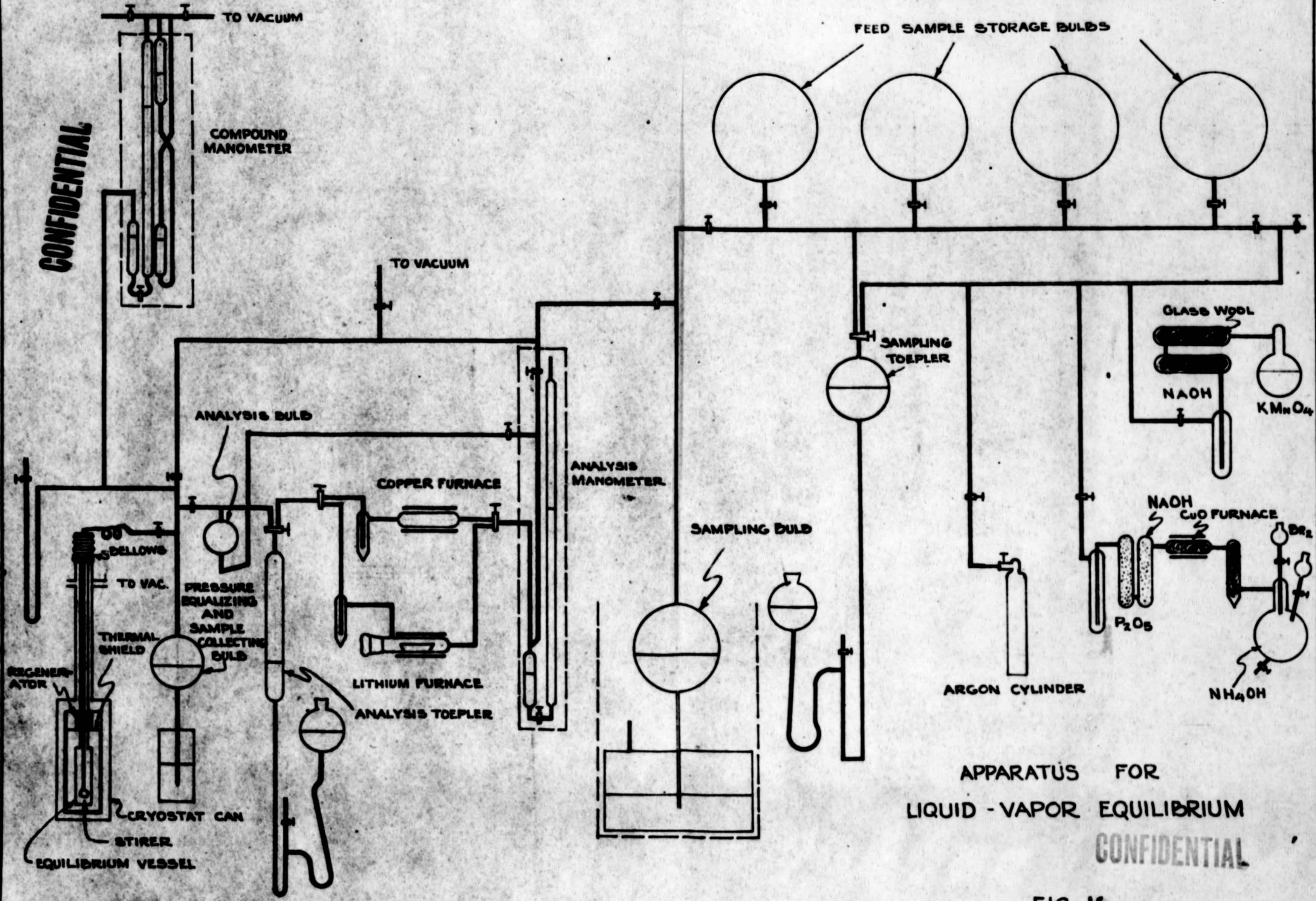

APPARATUS FOR
LIQUID - VAPOR EQUILIBRIUM

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FIG. 16

during vaporization can be held constant in this manner to a few millimeters of mercury pressure.

Temperature and Pressure Measurements

The temperature of the equilibrium vessel is measured by means of the two copper-constantan thermocouples in a well at the bottom of the equilibrium vessel. The indications of the termocouples are read on one of the Cryogenic Laboratory White double potentiometers (100,000 microvolt range) with which the EMF can be read to 0.04 microvolts (this corresponds to .003°K in the range of the air system measurements). Air saturated, finely shaved distilled water ice is used at all times for the cold junctions of the termocouples. The standard cell of the potentiometer is checked frequently against thermostated saturated cells which are the Cryogenic Laboratory standards.

The termocouples were calibrated against oxygen vapor pressures. Below one atmosphere, the equation of Cath[18]

$$\mathrm{Log}_{10}\ P_{atm} = -(419.31/T) + 5.2365 - 0.00648T$$

with the corrections to it found by Aston, Willihngans, and Messerly[19], was used in converting from oxygen vapor pressure temperatures to temperatures on the thermodynamic scale. Above one atmosphere, the equation of Dodge and Davis[20]

$$\mathrm{Log}_{10}\ P_{atm} = 5.76331 - 853.522/T + 54372.3/T^2 - 1783500/T^3$$

was used. The equation of Dodge and Davis gives 90.2° for the normal boiling point of oxygen which is in perfect agreement with the value accepted by the Cryogenic Laboratory.

Table XVI gives conversion tables for EMF to temperatures as determined from the oxygen vapor pressures that were used in all of these equilibrium studies.

Pressure was read by a Gaertner Cathetometer on the compound mercury manometer shown in figure 16. The manometer is of the same general design used by Kammerlingh-Onnes in state data studies[13] at the University of Leiden. It consists of two manometers in series, the first attached directly to the equili-

26a

TABLE XVI

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Calibration of Thermocouples

for Liquid-Vapor Equilibrium Apparatus

MV	°K	Δ
5500	64.29	71
90	65.00	71
80	65.71	71
70	66.42	70
60	67.12	70
5450	67.82	70
40	68.52	70
30	69.21	69
20	69.91	69
10	70.60	69
5400	71.29	68
90	71.97	67
80	72.64	66
70	73.30	66
60	73.96	66
5350	74.62	65
40	75.27	64
30	75.91	64
20	76.55	64
10	77.19	63
5300	77.82	63
90	78.45	63
80	79.08	62
70	79.70	62
60	80.32	62
5250	80.94	61
40	81.55	61
30	82.16	61
20	82.76	60
10	83.36	60
5200	83.96	60
90	84.56	60
80	85.16	60
70	85.76	59
60	86.35	59
5150	86.94	59
40	87.53	59
30	88.12	58
20	88.70	58
10	89.28	58
5100	89.86	57
90	90.43	57
80	91.00	57
70	91.57	57
60	92.14	57
5050	92.71	57
40	93.28	57
30	93.85	56
20	94.41	56
10	94.97	56
5000	95.53	56
90	96.09	56
80	96.65	56
70	97.21	56
60	97.77	56
4950		

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brium system and the second attached to the long arm of the first manometer. In this way, the sum of the pressures read on the two manometers gives the total pressure of the system.

The cathetometer is equipped with a steel scale and vernier which allows an interpolation of .05 mm. to be made on the main scale. The cathetometer scale was calibrated every 10 mm. against a silver inlaid scale of the Cryogenic Laboratory which had been originally calibrated at the National Bureau of Standards. The calibration corrections along with the corrections for depression of the mercury column from meniscus height, gravity correction on the mercury column, and temperature correction on the mercury column are given in table XVII.

The Analytical Apparatus

The analyses are made by a dry method and are taken at constant volume. The analysis apparatus is shown in figure 16 and is incorporated into the main lines of the apparatus.

The gas is circulated over the absorbent by means of a Toepler pump and finally returned to the original confining vessel at the original volume by means of this same pump. The pressure is then read and compared with the pressure of the original sample. For this purpose, the pressures are read on a mercury manometer using the Gaetner cathetometer. Fine copper screening rolled into small cylinders and heated in a furnace to 500°C is used for absorbing the oxygen. This is better than finely divided copper which eventually fuses to a solid mass of low rate of absorption. A liquid air trap is used to absorb any water vapor arising from hydrogen absorbed by the copper. Molten lithium at 300°C is used in the same way for the absorption of the nitrogen. In this manner, duplicate analyses agreeing to better than 0.05 per cent are obtained regularly.

The Gas Generation Equipment

The samples of oxygen and argon were as described in Part II of this report.

Nitrogen was prepared by the action of bromine on ammonia by a method similar to that described by Giauque[21]. Concentrated bromine water, made by dissolving bromine in a saturated KBr solution, is added hrough a stopcock to a six molal ammonium hydroxide solution in a two liter flask. Excess solution was removed through an additional stopcock sealed into the bottom of the flask. Ammonium hydroxide was added, as needed, through a separate stopcock, thus making the generation continous. The nitrogen passed through a copper oxide furnace heated to 450°C for removing ammonia, then through a large sodium hydroxide drier and three large driers containing phosphorus pentoxide, all in series. The gas finally passed through a liquid air trap. The nitrogen thus made was added to the feed mixture by means of the sampling Toepler shown in figure 16. Analysis of nitrogen made in this way gave 0.02 per cent oxygen and a trace of inert gas. The slight contamination is probably due to air dissolved in the ammonium hydroxide and bromine water.

At first an attempt was made to prepare nitrogen by heating ammonium dichromate. Fortunately, as a precaution, only a small quantity (5 grams) was used for a violent explosion occurred in heating in a confined vessel. This method was therefore abandoned and we wish to go on record as WARNING AGAINST HEATING AMMONIUM DICHROMATE IN A CLOSED SPACE.

Operation of the Equilibrium Apparatus

The gases are generated as described and made up by pressure (on the analysis manometer) in the ten liter storage vessels to the desired concentration of the feed mixture. An analysis is made on the feed mixture for the purpose of checking both the analysis apparatus and the gas generation equipment. This check is necessary because it prevents the use of any feed mixtures which may have become contaminated through some unnoticed blunder.

The amount of feed mixture sample is determined by measuring the temperature and pressure of the gas contained in the large sampling bulb whose volume is known to ± 0.05 cc. (The line volumes on all sections of the equilibrium apparatus and lines have been determined with an accuracy of ± 0.05 cc. for any given section.) After the sample has been measured out, the stopcock to the equilibrium vessel whose temperature has been lowered to 58°K. When the sample has finished condensing, the residual pressure in the lines is read. Three fillings of the large sampling bulb give a sample of approximately 0.36 moles in the equilibrium apparatus.

The temperature of the sample is slowly raised from 58°K to the desired temperature of the equilibrium measurement and then the manometer contacts are set for regulation. The bellows-stirrer is turned on and the sample allowed to vaporize very slowly and uniformly over a period of from one to two hours. Vaporization is allowed to take place until approximately 0.02 moles (500 cc at 1 atm) have been accumulated in the vapor phase. To ensure equilibrium the bellows stirrer is allowed to continue its action for another one and a half hours. During the periods of vaporization, stirring and standing, the filling tube is kept 0.3° - 0.5°K warmer than the equilibrium vessel. One-half hour after the bellows stirrer has been turned off, pressure and temperature measurements are taken and the stopcock between the equilibrium vessel and vaporization bulb are then analysed.

Sample Data:

Below are given the actual experimental data transcribed from our standard notebooks.

Page No. 8

Date 8/29/43

Feed Mixture No. 7 (for run 14)

Stored in Bulb No. 1

Partial pressure of O_2

T Bath ______ T Bulb 24.0 T_2 23.0 T_3 22.5 T_4 ______

Volume set at ______ mark on calibrated bulb.

T_2 = Upper Manometer

T_3 = Lower Manometer

Meniscus top		Meniscus bottom	
Scale	Vernier	Scale	Vernier
104	75	103	00
833	10	832	00
104	70	103	00
833	15	832	00

Partial pressure of O_2 + A

T Bath ______ T Bulb 24.0 T_2 23.0 T_3 22.6 T_4 ______

Volume set at top mark on calibrated bulb.

Meniscus top		Meniscus bottom	
Scale	Vernier	Scale	Vernier
88	25	86	35
938	70	937	50
88	30	86	60
938	60	937	40

Page No. 47

Date 8/31/43

System A - O_2 Run No. 14

Analysis of Feed Mixture for Oxygen

Total Initial pressure.

T bath 26.2 T_1 27.0 T_2 26.5 T_3

T_1 = Upper manometer

T_2 = Lower manometer

Meniscus top		Meniscus bottom	
Scale	Vernier	Scale	Vernier
127	20	125	60
578	90	577	80
127	20	125	40
578	95	577	70

Argon partial pressure.

T bath 26.8 T_1 --- T_2 27.8 T_2

	Meniscus top		Meniscus bottom	
	Scale	Vernier	Scale	Vernier
1st absorption	126	55	124	75
	191	70	190	30
2nd absorption	126	55	124	85
	191	70	190	10

1st Insertion

Page No. 39

Date 8/31/43

System $A - O_2$ Run No. 14

Measurement of amount of material in large vaporization bulb for Feed sample

Regulating manometer set at --- inches

Vaporization bulb initially at 3 mark on bottom

Vaporization bulb finally at 3 mark on bottom

T bath 4.585 T_1 25.5 T_2 27.2 T_3 26.5

T_1 = lines

T_2 = Upper manometer

T_3 = Lower manometer

Meniscus top		Meniscus bottom	
Scale	Vernier	Scale	Vernier
98	70	96	80
885	80	984	20
98	65	96	70
885	80	884	20

System $A - O_2$ Run No. 14

Measurement of amount of material in lines for Feed sample residual

Regulating manometer set at --- inches

Vaporization bulb initially at 3 mark on top

Vaporization bulb finally at 3 mark on top

T bath --- T_1 25.4 T_2 --- T_3 26.6

Meniscus top		Meniscus bottom	
Scale	Vernier	Scale	Vernier
108	40	106	90
117	30	116	45
108	35	106	90
108	40	106	80
117	30	116	45

2nd Insertion

Page No. 40

Date 8/31/43

System A - O$_2$ Run No. 14

Measurement of amount of material in large vaporization bulb for Feed Sample.

Regulating manometer set at --- inches.

Vaporizarion bulb initially at 4 mark on bottom

Vaporization bulb finally at 4 mark on bottom

T bath 4.545 T$_1$ 25.1 T$_2$ 27.0 T$_3$ 26.2

Meniscus top		Meniscus bottom	
Scale	Vernier	Scale	Vernier
120	70	118	95
810	70	809	50
120	65	118	80
810	70	809	50

System A - O$_2$ Run No. 14

Measurement of amount of material in lines for Feed sample residual

Regulating manometer set at --- inches

Vaporization bulb initially at 3 mark

Vaporization bulb finally at 3 mark

T bath --- T$_1$ 25.2 T$_2$ --- T$_3$ 26.3

Meniscus top		Meniscus bottom	
Scale	Vernier	Scale	Vernier
123	10	121	72
132	00	121	00

3rd Insertion

Page No. 41

Date 8/31/43

System $A - O_2$ Run No. 14

Measurement of amount of material in large vaporization bulb for Feed sample.

Regulating manometer set at --- inches

Vaporization bulb initially at 3 mark on bottom

Vaporization bulb finally at 3 mark on bottom

T bath 4.400 T_1 24.8 T_2 26.8 T_3 26.0

Meniscus top		Meniscus bottom	
Scale	Vernier	Scale	Vernier
113	65	112	00
694	00	693	10
113	95	112	20
694	10	692	95

System $A - O_2$ Run No. 14

Measurement of amount of material in lines for Feed sample residual

Regulating manometer set at inches

Vaporization bulb initially at 3 mark on top

Vaporization bulb finally at 3 mark on top

T bath --- T_1 24.8 T_2 --- T_3 26.0

Meniscus top		Meniscus bottom	
Scale	Vernier	Scale	Vernier
118	95	117	00
127	85	127	30

Page No. 29

DATE 8/31/43

TIME 5:07 P. M.

System A - O_2 Run No. 14

Thermometers before:

No. 1 28.8 No. 2 28.5 No. 3 28.1 No. 4

No. 5 No. 6 No. 7

Thermometers after:

No. 1 28.8 No. 2 28.5 No. 3 28.0 No. 4

No. 5 No. 6 No. 7

T_1 = Upper manometer

T_2 = Lower manometer

T_3 = Small vaporization bulb

Collimation readings (50 cms on glass scale)

	Scale	Vernier
Upper telescope	786	25
Lower telescope	786	25
Upper telescope	690	10
Lower telescope	690	15

Page No. 30

Date 8/31/43

Time 5:07 P. M.

	Meniscus bottom			Meniscus top		
	Time	Scale	Vernier	Time	Scale	Vernier
Lower arm	0.8	24	90	0.3	26	25
Upper arm	2.2	800	45	1.5	801	60
Lower arm (c)	3.2	37	50	2.8	39	00
Upper arm (c)	4.2	772	35	3.9	773	55

	Meniscus bottom			Meniscus top		
	Time	Scale	Vernier	Time	Scale	Vernier
Lower arm	5.6	25	00	5.0	26	00
Upper arm	6.8	800	65	6.3	801	50
Lower arm (c)	7.8	37	60	7.4	38	95
Upper arm (c)	8.7	772	25	8.4	773	60

	Meniscus bottom			Meniscus top		
	Time	Scale	Vernier	Time	Scale	Vernier
Lower arm	9.8	25	00	9.2	26	20
Upper arm	10.7	800	60	10.1	801	30
Lower arm (c)	12.0	37	65	11.5	39	25
Upper arm (c)	13.0	772	15	12.5	773	60

	Meniscus bottom			Meniscus top		
	Time	Scale	Vernier	Time	Scale	Vernier
Lower arm						
Upper arm						
Lower arm (c)						
Upper arm (c)						

Page No. 29

Date 8/31/43

Time 5:07 P. M.

System A - O_2 Run No. 14

Condition of ice junctions 1 hrs in use. Standard cell No. Eo.26129

Standard cell setting 1.01895 Volts

Before U 43.1 cms L 43.3 cms Z 43.1 cms

After U 43.4 cms L 43.6 cms Z 43.5 cms

Thermocouples at beginning

Time -5.0 Can top 4650 Can bottom 5150

	Time	Potentiometer	cm	cm(chk)
	-4.0	4970	62.2	
Shield Top		80	35.1	42.0
	-3.0	5110	67.4	
Shield Bottom		20	40.2	41.9
	-2.0	4970	63.3	
Tube Couple No.1		80	36.3	42.0
	-1.0	4660	48.9	
Tube Couple No.2		70	21.6	42.1

Thermocouples at end

Time 12.0 Can top 4660 Can bottom 5120

	Time	Potentiometer	cm	cm(chk)
	13.0	4970	64.3	
Shield Top		80	37.0	42.6
	14.0	5110	50.8	
Shield Bottom		20	23.6	42.7
	15.0	4970	62.5	
Tube Couple No.1		80	35.4	42.7
	16.0	4650	60.1	
Tube Couple No. 2		60	43.8	42.8

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Date 8/31/43

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Equilibrium Vessel Temperatures

Couple No. 1				Couple No. 2			
Time	Potentiometer	cm	cm(chk)	Time	Potentiometer	cm	cm(chk)
0.5	4980	45.7	42.1	1.0	4980	45.9	42.1
2.0	4980	45.7	42.1	2.5	4980	45.9	42.1
3.0	4980	45.7	42.2	3.5	4980	45.9	42.1
4.0	R 4980	45.7					
	4990	18.2	42.1				
5.0	R 4990	67.8					
	4980	39.3	42.5				
7.0	R 4980	45.8	42.4	7.5	4980	45.7	42.4
8.0	4980	45.8	42.4	8.5	4980	45.7	42.4
9.0	4980	46.0	42.5	9.5	4980	45.7	42.3
10.0	4980	46.1	42.5				

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Page No. 42

Date 8/31/43

System A - O_2 Run No. 14

Measurement of amount of material in small vaporization bulb for material balance

Regulating manometer set at + 1.7 inches

Vaporization bulb initially at 4.2 mark on bottom

Vaporization bulb finally at 4.2 mark on bottom

T bath 28.0 T_1 28.8 T_2 28.6 T_3

T_1 = Upper manometer

T_2 = Lower manometer

Meniscus top		Meniscus bottom	
Scale	Vernier	Scale	Vernier
28	20	26	80
690	80	689	65
28	25	26	90
690	85	689	60

Page No. 45

Date 8/31/43

System A - O_2 Run No. 14

Analysis of Equilibrium Vapor for Oxygen

Total Initial pressure

T bath 28.0 T_1 27.8 T_2 27.2 T_2

Meniscus top Scale	Meniscus top Vernier	Meniscus bottom Scale	Meniscus bottom Vernier
125	65	123	70
638	05	636	85
125	55	124	00
638	10	636	70
125	60	124	00

Argon Partial pressure

T bath 27.0 T_1 --- T_2 26.4 T_3

	Meniscus top Scale	Meniscus top Vernier	Meniscus bottom Scale	Meniscus bottom Vernier
1st absorption	129	40	127	65
	224	15	223	00
2nd absorption	130	00	128	10
	223	90	222	35
3rd absorption	130	05	128	25
	224	00	222	00
	130	05	128	30
	224	00	222	05

Sample Calculations

Below are described the calculations of the data given in the previous section.

The calculation of the composition of the feed mixture from the data taken during its preparation is summarized below:

Partial Pressure of A and O_2		Partial Pressure of O_2
938.65	Height of Hg in long arm	833.10
-88.30	Height of Hg in short arm	-104.70
850.35	Uncorrected pressure	728.40
+0.23	Meniscus correction on long arm	+0.22
-0.33	Meniscus correction on short arm	-0.33
-0.40	Gravity correction on total P	-0.40
-3.72	Temperature correction on total P	-3.17
-0.10	Scale calibration on short arm	-0.05
+0.12	Scale calibration on long arm	+0.12
846.08	Corrected pressure in mm of Hg	724.79

(see Table XVII for corrections applied above)

(846.03-724.79)/846.08 = .1434 mole fraction Argon

The calculation of the composition of the feed mixture from the analyses follows:

Total initial pressure (oxygen and argon) calculated in the same manner as above - 449.20mm

Partial pressure of argon - 64.79mm

Correcting for temperature change in the analysis bulb and for the volume change due to the difference in heights of the short arm of the manometer

$$64.79 \times 299.4/300.0 \times \frac{306.4 + 0.4}{306.4 + 0.4} = 64.66\text{mm}$$

64.66/449.20 = .1439 mole fraction of argon

Averaging the above data, composition of feed mixture = .1437 mole fraction of argon. This serves as a check on the preparation of the sample.

The calculation of the quantity of feed sample introduced

41a

TABLE XVII

MANOMETRY CORRECTIONS FOR EQUILIBRIUM APPARATUS

1. Scale corrections (at 0°C.)

Interval	Correction (to be added)	Interval	Correction (to be added)
0 - 50	.10	500 - 550	.18
50 - 100	.07	550 - 600	.18
100 - 150	.05	600 - 650	.15
150 - 200	.10	650 - 700	.12
200 - 250	.10	700 - 750	.12
250 - 300	.10	750 - 800	.10
300 - 350	.07	800 - 850	.12
350 - 400	.07	850 - 900	.12
400 - 450	.05	900 - 950	.12
450 - 500	.15	950 - 1000	.12

II. Gravity correction

$\Delta P = (-.000551)P$

III. Temperature correction
(For mercury column and scale simultaneously to 0°C.)

$\Delta P = (-19.2 \times t\ ^{\circ}C.)P$

IV. Meniscus Height corrected (to be added)

Meniscus Height

	.5	.6	.7	.8	.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8
Correction	.10	.12	.13	.15	.17	.19	.21	.23	.25	.27	.29	.31	.33	.34

into the equilibrium vessel is made from the necessary data given in pages (32), (33), and (34), and is summarized below:

First portion (page 32) Pressure = 782.60mm

Material in lines and large sampling bulb originally

3149.2cc at 298.995°K (sampling bulb and ends all in bath)

56.6cc at 298.6°K (other sections of line involved)

Total number of moles in bulb and lines

$$N_m = 782.60 \ (3149.2/298.995) + (56.6/298.7) \ 1.60345 \times 10^{-5}$$
$$= 0.135472 \text{ moles}$$

Residual material after condensation

55.2cc at 298.6°K Pressure = 8.72mm

Total number of moles remaining in lines

$$N_r = 8.72(55.2/298.6)1.60345 \times 10^{-5} = 0.000026 \text{ moles}$$

Material actually condensed in equilibrium vessel plus vapor remaining beyond stopcock for first insertion

$$N_1 = N_m - N_r = 0.135472 - 0.000026 = 0.135446 \text{ moles}$$

Second portion (page 33)

Calculations exactly as described above

$$N_2 = 0.117881 - 0.000025 = 0.117856 \text{ moles}$$

Third portion (page 34)

Calculations exactly as described above

$$N_3 = 0.099193 - 0.0000025 = 0.099168 \text{ moles}$$

Total number of moles of feed sample

$$N_{total} = N_1 + N_2 + N_3 = 0.135446 + 0.117856 + 0.099168$$
$$= 0.352470$$

The Equilibrium Measurements

The data for the temperature and pressure measurements appear on pages (35), (36), (37) and (38). The temperature is calculated using Table I and the pressure is calculated in an identical manner as those on page (41).

Corrected pressure = 1500.7mm Temperature = 96.58°K

The calculation of the material balance to obtain the composition of the equilibrium liquid follows:

V/T sums up to stopcock (stopcock seperating equilibrium vessel and bellows mechanism from vaporization bulb and lines)

$$\frac{(35.6 - 10.4)\text{cc}}{96.58^\circ\text{K}} = 0.26209 \text{ cc}/^\circ \text{ (vapor in equilibrium vessel)}$$

$$\frac{24.0}{(301.2 - 96.58)/2} - 0.12079 \text{ cc}/^\circ \text{ (vapor in filling line)}$$

$$\frac{24.3}{301.2} = 0.08068 \text{ cc}/^\circ \text{ (vapor in bellows and connecting line)}$$

$$\text{Sum} = 0.46356 \text{ cc}/^\circ$$

Total number of moles in vapor phase up to the stopcock

$$N_a = 0.46356 \times 1500.7 \times 1.60345 \times 10^{-5} = 0.011155$$

$$\text{Where } 1.60345 \times 10^{-5} = \frac{1}{760 \times R} = \frac{1}{760 \times 82.06}$$

<u>V/T sums beyond stopcock (page 42)</u>

523.6 cc vaporization bulb
1.1 cc from vapor. bulb to trap
13.7 cc to top of regulating manometer and compound manometer
3.7 cc regulating manometer
1.7 cc compound manometer
543.8 cc at 301.2°K and 658.45 mm

Total number of moles in vapor phase beyond stopcock

$$N_b = \frac{658.45 \times 543.8 \times 1.60345 \times 10^{-5}}{301.2} = 0.019062 \text{ moles}$$

Total number of moles in vapor phases

$$N_v = N_a + N_b = 0.011155 + 0.019062 = 0.030217 \text{ moles}$$

Analysis of vapor (page 43) is 0.1837 mole fraction argon

The completion of this calculation is made in Table XVIII which is a standard form for presenting the equilibrium data taken on this apparatus.

TABLE XVIII

Run No. 14

Temperature 96.58 °K

Date 8/31/43

Pressure 1500.7 mm

System A - O_2

Hours for Vaporization 1.5

Hours Standing 1.5

Feed Mixture: 0.352470 mols at 85.63 %O_2, 14.37 %A, 0 %N_2

Equilibrium Vapor: 0.030217 mols at 81.63 %O_2, 18.37 %A, 0 %N_2

Material Balance

	Mols O_2	Mols A	Mols N_2	Total
Feed Mixture	0.301820	0.050650	0	0.352470
Equilibrium Vapor	0.024666	0.005551	0	0.030217
Equilibrium Liquid	0.277154	0.045099	0	0.322253

Equilibrium Liquid: 86.01 %O_2, 13.99 %A, 0 %N_2

Equilibrium Vapor Corrected to 1520 mm

81.65 %O_2, 18.35 %A, 0 %N_2

Equilibrium Temperature Corrected to 1520 mm: 96.72 °K

$K_{O_2} = \frac{81.65}{86.01} = 0.9493$, $K_A = \frac{18.35}{13.99} = 1.312$, $K_{N_2} =$ _____ $=$ _____

DATA

DATA ON THE SYSTEM ARGON-OXYGEN TO A PRESSURE OF TWO ATMOSPHERES

In view of the doubt cast upon the data of Bourbo and Ishkin above one atmosphere (see Page 7, Part I), it seemed most advisable to check this region because it is the most important one in the production of pure oxygen. Accordingly, points were taken below 50 per cent argon concentration from one to two atmospheres pressure.

Table XIX is a summary of the equilibrium data as actually obtained experimentally. Column one gives the mole percent argon in the liquid; column two gives the mole percent argon in the vapor; column three is the pressure of the actual measurement; column four is the temperature corresponding to P; while column five is the equilibrium constant, $K = y/x$, at the pressure, P, of column three and at the temperature, T, of column four. Table XX is the above data corrected to one, one and a half or two atmospheres pressure as the case may be. The columns of Table XX correspond to the columns of Table XIX. Table XXI contains the smoothed values of y (mole fraction in the vapor) and K (mole fraction in the vapor/mole fraction in the liquid) up to 0.50 mole percent for argon in the argon-oxygen system at two atmospheres. Table XXII contains the smoothed values of y and K at values of x up to 0.50 mole percent for argon in the argon-oxygen system at 96°K. In correcting the individual points to 96°K, the relationship

$$P_1\ (96^\circ K) = P_1^\circ\ (96^\circ K) P_1(T)/P_1^\circ\ (T) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (32)$$

where P_1 (96°K) = partial pressure of argon at 96°K

P_1° (96°K) = vapor pressure of pure argon liquid at 96°K

P_1 (T) = partial pressure of argon at the temperature measured

P_1° (T) = vapor pressure of pure argon liquid at the temperature measured

was used.

TABLE XIX

EQUILIBRIUM DATA IN THE SYSTEM ARGON-OXYGEN

Mole percent argon in liquid x	Mole percent argon in vapor y	Pressure P (mm)	Temperature T (°K)	Equilibrium Constant K = y/x
4.86	6.81	1542.0	97.45	1.401
4.99	7.36	747.70	90.09	1.475
13.99	18.37	1500.7	96.58	1.313
13.84	18.95	1010.7	92.34	1.369
23.31	29.79	1428.5	95.64	1.278
23.77	32.58	774.65	89.27	1.371
34.26	40.75	1519.5	95.86	1.189

TABLE XX

EQUILIBRIUM DATA IN THE SYSTEM ARGON-OXYGEN

Mole percent argon in liquid y	Mole percent argon in vapor x	Pressure P (mm)	Temperature T (°K)	Equilibrium Constant K = y/x
4.86	6.82	1520	97.13	1.403
4.99	7.36	760	89.92	1.475
13.99	18.35	1520	96.72	1.312
13.84	18.93	1034	96.72	1.368
23.31	29.72	1520	96.19	1.275
23.77	32.62	760	89.01	1.372
34.26	40.75	1520	95.86	1.189

TABLE XXI

SMOOTHED VALUES OF EQUILIBRIUM DATA FOR THE SYSTEM ARGON OXYGEN AT TWO INT. ATM.

Mole Percent Argon in Liquid x	Mole Percent Argon In Vapor y	K (y/x)
0	0	(1.386)
2	2.75	1.377
5	6.82	1.364
10	13.41	1.341
15	19.74	1.316
20	25.78	1.289
25	31.48	1.259
30	36.69	1.223
40	46.16	1.154
50	55.65	1.113

TABLE XXII

SMOOTHED VALUES OF EQUILIBRIUM DATA FOR THE SYSTEM ARGON-OXYGEN AT 96.00°K

Mole Percent Argon In Liquid x	Mole Percent Argon In Vapor y	K (y/x)
0	0	(1.453)
2	2.90	1.450
5	7.22	1.444
10	14.31	1.431
15	20.48	1.365
20	26.20	1.310
25	31.53	1.261
30	36.58	1.219
40	46.35	1.159
50	55.72	1.114

Table XXIII gives the results of the Duhem calculation on the isotherm at $96^{\circ}K$. The agreement is very satisfactory in view of the fact that the points were taken at two atmospheres and had to be extrapolated to $96^{\circ}K$ by means of equation (32).

Figure 17 is a graph of K versus x for the isobars at 14.7, 20 and 29.4 lbs./in^2 abs in the system argon-oxygen. The 14.7 lbs./in^2 abs curve is that taken in isothermal calorimeter "C" of Part II with two additional points when in the present apparatus while the 20 and 29.4 lbs./in^2 abs curves are those determined in the new equilibrium apparatus described in Part III. The region beyond 0.50 mol percent argon was extrapolated by paralleling the 14.7 lbs./in^2 abs curve.

Data on the System Nitrogen-Oxygen to a Pressure of Two Atmospheres

The data of Dodge and Dunbar give a fair fit with the Duhem equation. This system has been reinvestigated as a means of comparing the method of Dodge and Dunbar with our own. We believe that better data has resulted from the reinvestigation.

Table XXIV summarizes the data experimentally obtained. Column one gives the mole percent oxygen in the liquid; column two gives the mole percent oxygen in the vapor; column three is the pressure in millimeters of the experimental measurement; column four is the temperature observed in $^{\circ}K$ corresponding to the pressure given in column three; while column five is the equilibrium constant, $K = y/x$, at the pressure, P, of column three and at the temperature, T, of column four.

Table XXV is the above data smoothed to the $85.00^{\circ}K$ isotherm or to the one atmosphere or two atmospheres isobar. This was done exactly as described for the argon-oxygen system using equation (32). The columns of table XXV correspond to the columns of table XXIV.

TABLE XXIII

THIS RESEARCH A - O_2 ISOTHERM AT 96.00°K.

N_1 (N_2)	$a_1 = f/f_1^\circ$	a_1 (plot)	Percent Dev.
.98	0.9788	0.9800	- 0.12
.95	0.9481	0.9496	- 0.16
.90	0.8944	0.8987	- 0.48
.85	0.8468	0.8480	- 0.14
.80	0.8016	0.8018	- 0.03
.75	0.7576	0.7575	+ 0.02
.70	0.7137	0.7104	+ 0.47
.60	0.6226	0.6157	+ 1.11
.50	0.5267	0.5192	+ 1.42

FIGURE 17

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K-X DIAGRAM FOR THE SYSTEM
ARGON-OXYGEN

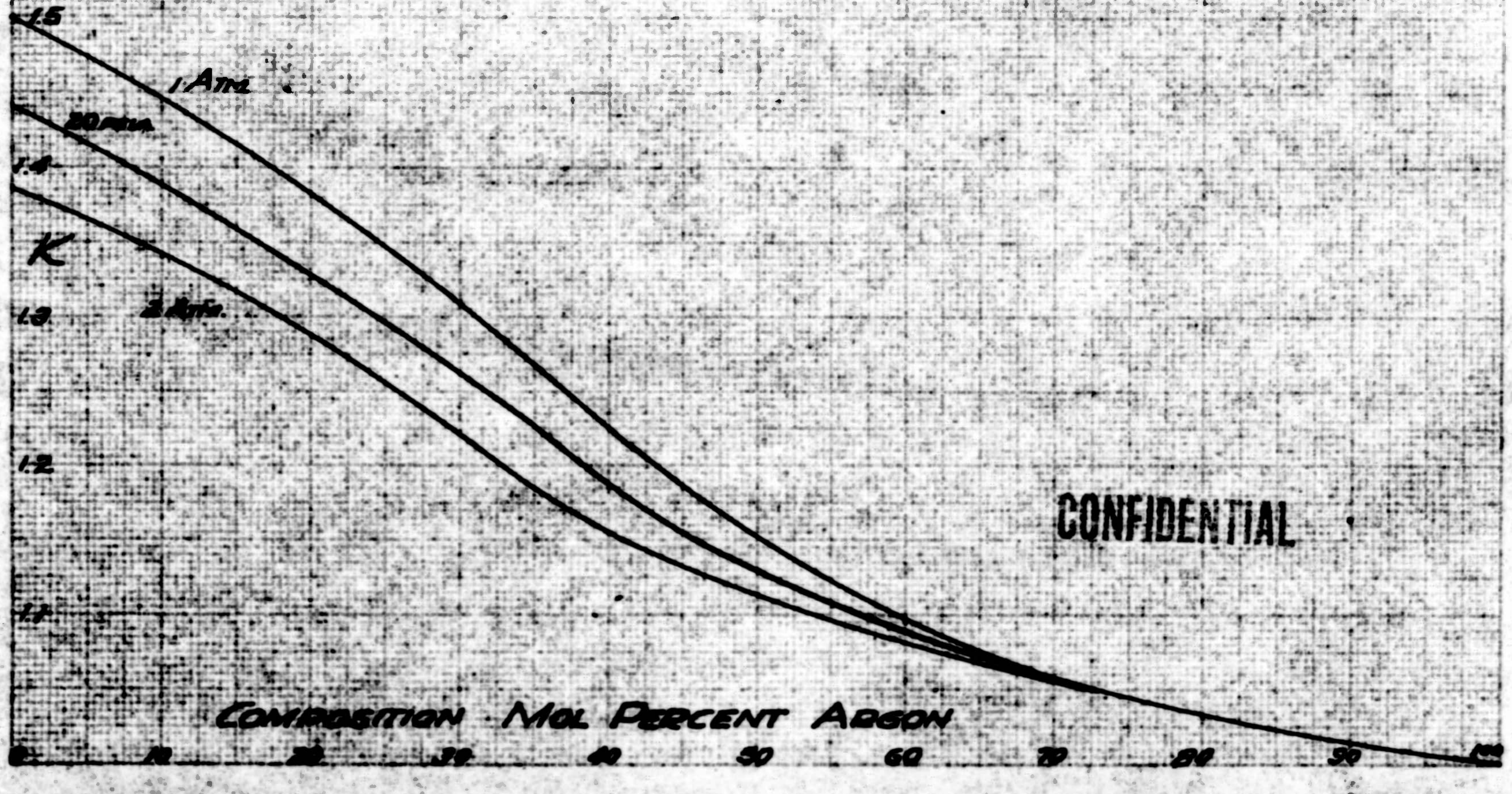

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TABLE XXIV

EQUILIBRIUM DATA IN THE SYSTEM NITROGEN-OXYGEN

Mole Percent Oxygen In Liquid x	Mole Percent Oxygen In Vapor y	Pressure P (mm)	Temperature T (°K)	Equilibrium Constant K = y/x
32.44	10.20	808.9	80.43	0.3144
33.99	12.73	1468.6	86.37	0.3745
48.84	21.80	1491.5	88.08	0.4464
50.98	20.83	1075.8	84.96	0.4086
53.25	21.35	786.6	82.23	0.4009
53.99	21.58	744.1	81.68	0.3997
61.63	27.21	810.3	83.34	0.4415
63.73	29.74	912.2	84.86	0.4667
74.60	40.29	726.1	84.31	0.5401
77.33	46.02	1426.9	91.78	0.5951
94.68	81.50	1539.6	96.27	0.8608
95.39	82.63	793.2	89.34	0.8662
95.91	82.58	475.9	84.84	0.8610

TABLE XXV

EQUILIBRIUM DATA IN THE SYSTEM NITROGEN-OXYGEN

Mole Percent Oxygen In Liquid x	Mole Percent Oxygen In Vapor y	Pressure P (mm)	Temperature T (°K)	Equilibrium Constant K = y/x
32.44	10.08	760	79.86	0.3107
33.99	12.81	1520	86.73	0.3769
33.99	12.40	1287.5	85.00	0.3648
48.84	21.85	1520	88.28	0.4474
50.98	20.84	1080.1	85.00	0.4088
53.25	21.22	760	81.91	0.3985
53.99	21.67	760	81.88	0.4014
61.63	26.96	760	82.74	0.4374
63.73	29.80	925.3	85.00	0.4676
74.60	40.36	760	84.75	0.5410
77.33	46.39	1520	92.49	0.6000
94.68	81.43	1520	96.12	0.8601
95.39	82.47	760	88.92	0.8646
95.91	82.63	484.5	85.00	0.8615

The data given in table XXV were plotted either at constant pressure or at constant temperature and the equilibrium constants were then read off at round values of oxygen and nitrogen concentrations. These are tabulated in tables XXVI - XXIX which are for the isobars at one atmosphere, 20 lbs./in^2 abs and two atmospheres and the isotherms at 85.00°K, respectively. Table XXX gives the result of the Duhem calculation performed on the data obtained at 85.00°K. In figures 18 - 23 are plotted the above data as follows: Fig. 18 is a plot of K vs x at one and two atmospheres and 20 lbs./sq. inch nitrogen; Fig. 19 is a plot of x and y vs T at one and two atmospheres and 20 lbs./sq. inch for oxygen and nitrogen; Fig. 20 is a plot of x and y vs y at one and two atmospheres for oxygen and nitrogen; Fig. 22 is a plot of partial pressures of oxygen and nitrogen vs mole percent oxygen in liquid at 85°K; and Fig. 23 is a plot of K vs x at 85°K for nitrogen.

From the equilibrium pressure, temperature, and concentration it was possible to obtain vapor pressure equations for various mixtures of oxygen and nitrogen between one and two atmospheres. These equations are of the form

$$\log_{10} P_{atm} = -\frac{A}{T} + B$$

where A and B are functions of the concentration. These different values of A and B are given in table XXXI. From table XXXI it was possible to calculate the boiling points of various mixtures of nitrogen and oxygen. Table XXXII gives the boiling point of nitrogen-oxygen mixtures at one and two atmospheres while table XXXIII gives the boiling points of mixtures of nitrogen and oxygen at 20 lbs./in^2 abs. Table XXXII contains several values obtained from the equations of Dodge and Dunbar for comparison. These are listed under the column headed D and D. Table XXXIV lists the total pressure above nitrogen-oxygen mixtures at 85°K.

Data on the System Oxygen-Nitrogen-Argon to a Pressure of Two Atmospheres

It was decided to obtain data on the system from one to two atmospheres

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TABLE XXVI

EQUILIBRIUM IN SYSTEM NITROGEN-OXYGEN AT ONE INT. ATM.

Mole Percent Oxygen In The Liquid x	Mole Percent Oxygen In The Vapor y	Equilibrium Constant K = y/x	Mole Percent Nitrogen In The Liquid x	Mole Percent Nitrogen In The Vapor y	Equilibrium Constant K = y/x
0	0		100.00	100.00	1.000
1	0.15	0.1500	99	99.85	1.009
2	0.43	0.2150	98	99.57	1.016
5	1.22	0.2440	95	98.78	1.040
10	2.66	0.2660	90	97.34	1.082
20	5.65	0.2825	80	94.35	1.179
30	9.11	0.3037	70	90.89	1.298
40	13.42	0.3355	60	86.58	1.443
50	18.90	0.3780	50	81.10	1.622
60	25.63	0.4272	40	74.37	1.859
70	34.88	0.4983	30	65.12	2.171
80	48.06	0.6008	20	51.94	2.597
90	67.42	0.7491	10	32.58	3.258
95	81.15	0.8542	5	18.85	3.770
98	91.69	0.9356	2	8.31	4.155
99	95.68	0.9665	1	4.32	4.320
100	100.00	1.0000	0	0	4.510

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TABLE XXVII

EQUILIBRIUM IN THE SYSTEM NITROGEN-OXYGEN AT 20 lbs/sq. in. ABS.

Mole Percent Oxygen In the Liquid x	Mole Percent Oxygen In the Vapor y	Equilibrium Constant K = y/x	Mole Percent Nitrogen In the Liquid x	Mole Percent Nitrogen In the Vapor y	Equilibrium Constant K = y/x
0	0		100	100.00	1.000
1	0.21	0.210	99	99.79	1.008
2	0.53	0.265	98	99.47	1.015
5	1.39	0.278	95	98.61	1.038
10	2.89	0.289	90	97.11	1.079
20	6.40	0.320	80	93.60	1.170
30	10.40	0.347	70	89.60	1.280
40	14.80	0.370	60	85.20	1.420
50	20.05	0.401	50	79.95	1.599
60	27.00	0.450	40	73.00	1.825
70	36.10	0.516	30	63.90	2.130
80	49.04	0.613	20	50.96	2.548
90	68.30	0.759	10	31.70	3.170
95	81.90	0.862	5	18.10	3.620
98	92.07	0.939	2	7.93	3.965
99	95.90	0.969	1	4.10	4.100
100	100.00	1.000	0	0	4.250

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TABLE XXVIII

EQUILIBRIUM IN THE SYSTEM NITROGEN-OXYGEN AT TWO INT. ATM.

Mole Percent Oxygen In the Liquid x	Mole Percent Oxygen In the Vapor y	Equilibrium Constant K = y/x	Mole Percent Nitrogen In the Liquid x	Mole Percent Nitrogen In the Vapor y	Equilibrium Constant K = y/x
0	0		100.00	100.00	1.000
1	0.26	0.2600	99	99.74	1.007
2	0.61	0.3050	98	99.39	1.014
5	1.61	0.3220	95	98.39	1.036
10	3.36	0.3360	90	96.64	1.074
20	7.09	0.3545	80	92.91	1.161
30	11.44	0.3813	70	88.56	1.265
40	16.00	0.4000	60	84.00	1.400
50	21.90	0.4380	50	78.10	1.562
60	28.76	0.4793	40	71.24	1.781
70	37.84	0.5406	30	62.16	2.072
80	50.62	0.6328	20	49.38	2.469
90	69.57	0.7730	10	30.43	3.043
95	82.85	0.8721	5	17.15	3.430
98	92.57	0.9446	2	7.43	3.715
99	96.17	0.9714	1	3.83	3.830
100	100.00	1.0000	0	0	3.943

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TABLE XXIX

EQUILIBRIUM IN THE SYSTEM NITROGEN-OXYGEN AT 85°K.

Mole Percent Oxygen In the Liquid x	Mole Percent Oxygen In the Vapor y	Equilibrium Constant K = y/x	Mole Percent Nitrogen In the Liquid x	Mole Percent Nitrogen In the Vapor y	Equilibrium Constant K = y/x
0	0		100.00	100.00	1.0000
1	0.32	0.321	99	99.68	1.0073
2	0.64	0.324	98	99.36	1.0141
5	1.64	0.328	95	98.36	1.0356
10	3.37	0.337	90	96.63	1.0737
20	7.01	0.3505	80	92.99	1.162
30	10.62	0.3540	70	89.36	1.277
40	14.99	0.3747	60	85.01	1.417
50	20.40	0.4080	50	79.60	1.592
60	26.82	0.4470	40	73.18	1.830
70	35.71	0.5101	30	64.29	2.143
80	48.21	0.6026	20	51.79	2.590
90	67.19	0.7466	10	32.81	3.281
95	80.31	0.8454	5	19.69	3.938
98	91.01	0.9287	2	8.99	4.495
99	95.42	0.9638	1	4.58	4.580
100	100.00	1.0000	0	0	

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TABLE XXX

DUHEM CALCULATION ON NITROGEN-OXYGEN MIXTURE AT 85°K.

N_1 Mole Fraction Nitrogen In Liquid	a_1 (plot)	$a_1 = \frac{f_1}{f_1^0}$	Percent Dev.
1.00	1.0000	1.0000	0
.99	.9900	.9901	.01
.98	.9800	.9806	.06
.95	.9501	.9515	.15
.90	.9005	.9018	.14
.85	.8513	.8523	.12
.80	.8057	.8052	.06
.75	.7611	.7588	.30
.70	.7208	.7142	.92
.60	.6278	.6217	.98
.50	.5280	.5280	0
.40	.4316	.4347	.72
.30	.3263	.3328	1.97
.20	.2204	.2256	2.36
.10	.1078	.1155	6.70

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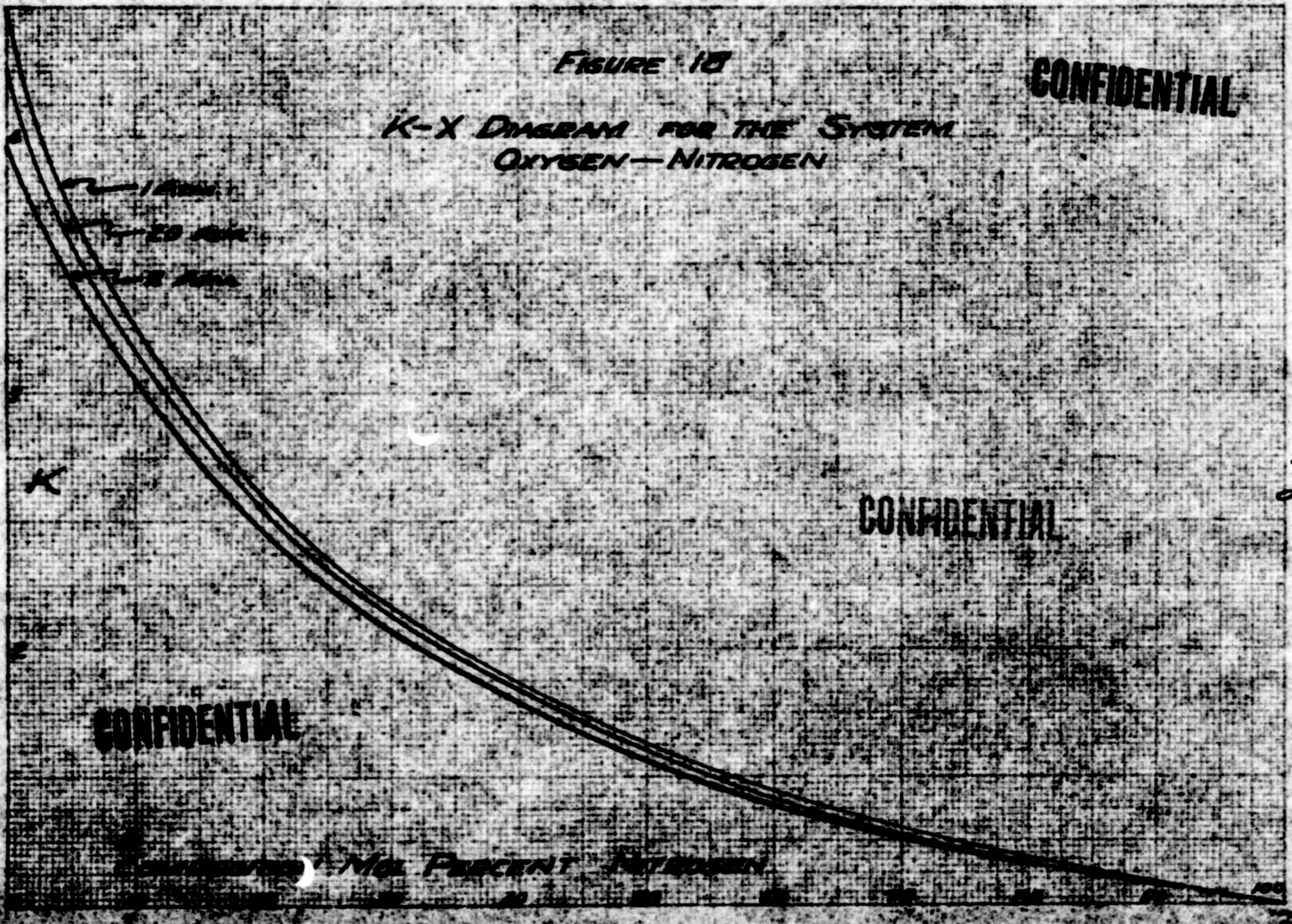

FIGURE 18

K-X DIAGRAM FOR THE SYSTEM
OXYGEN—NITROGEN

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Engraving, 10 × 15 in.
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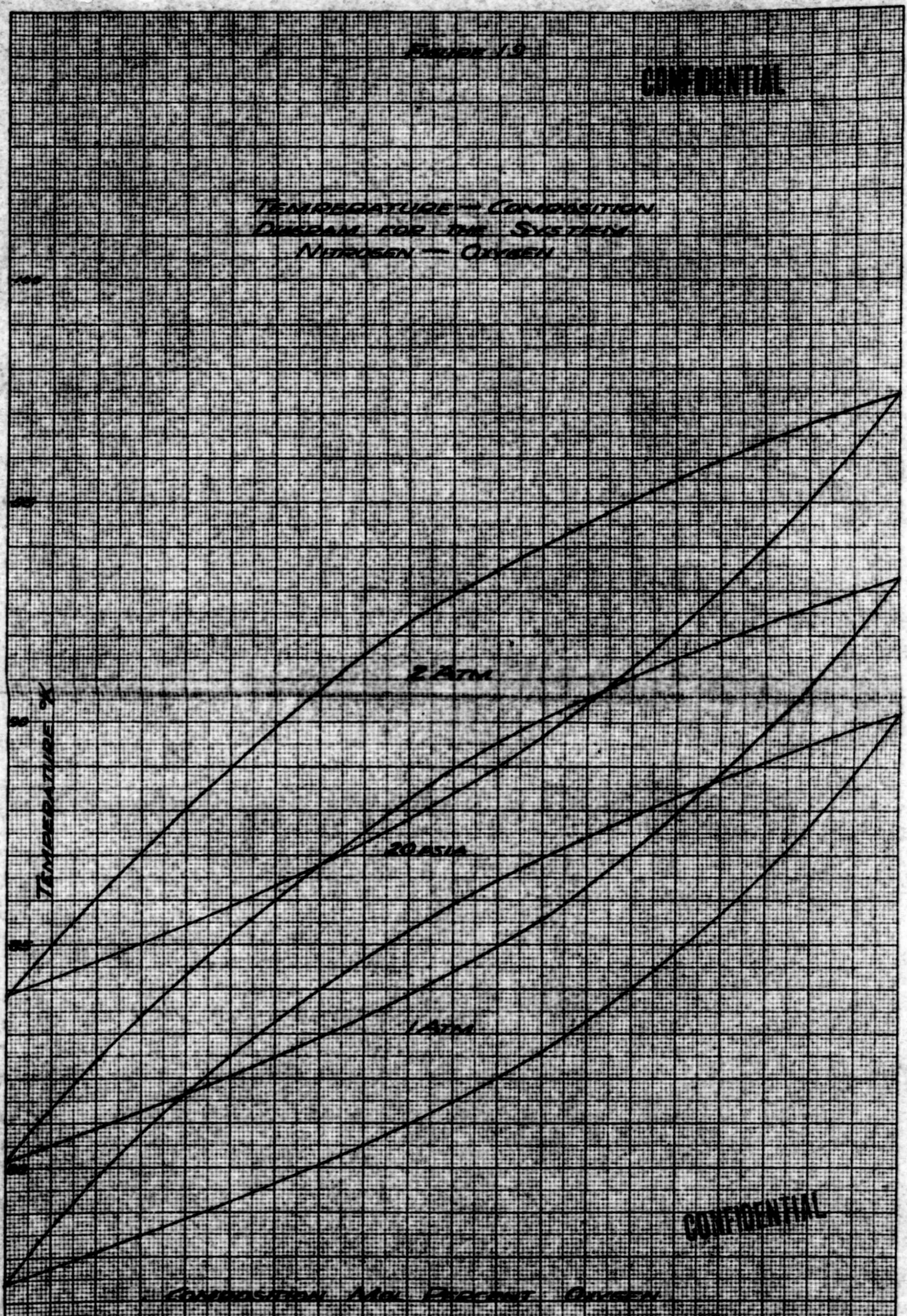

Figure 19

Temperature — Composition
Diagram for the System
Nitrogen — Oxygen

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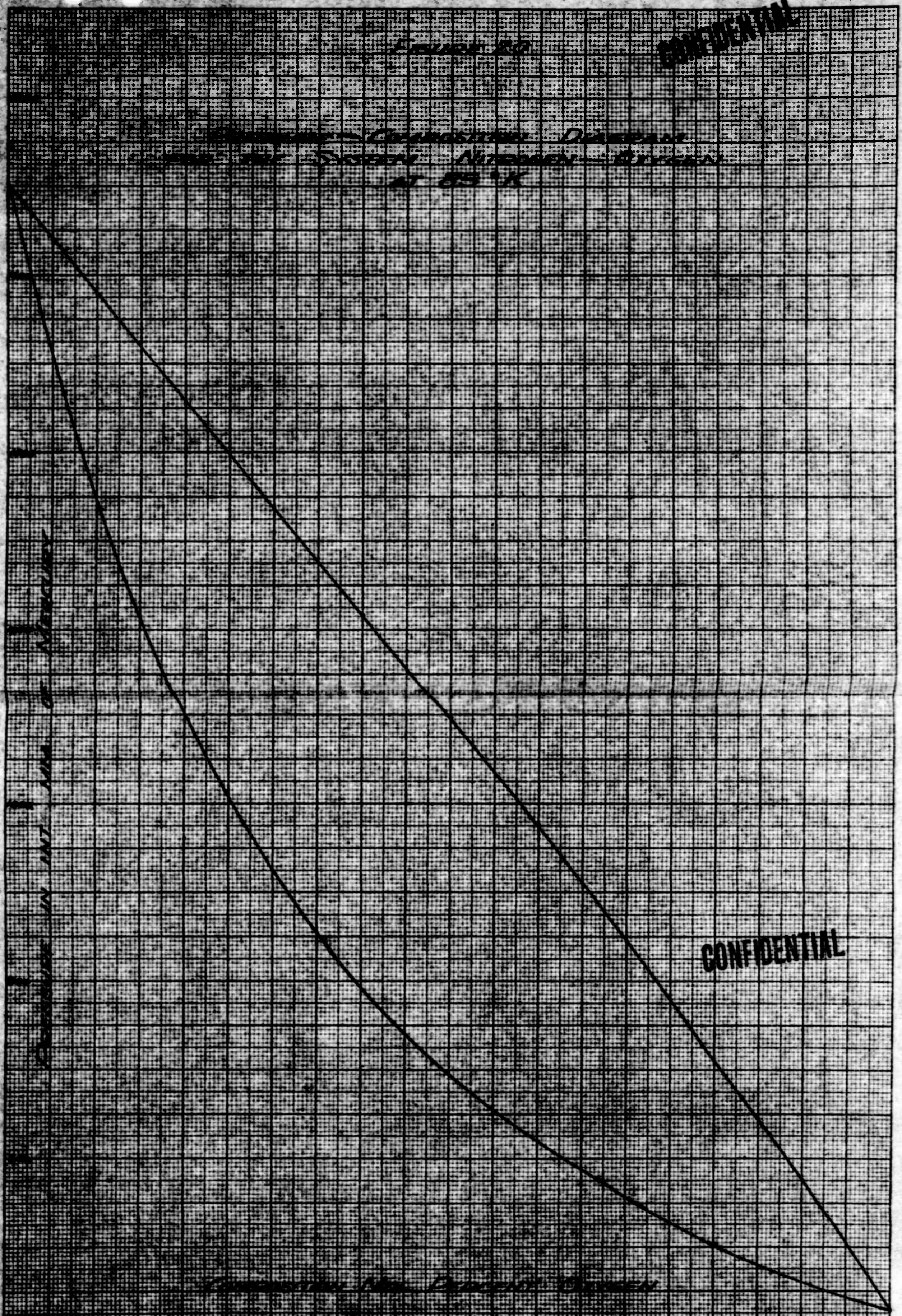

Figure 26

Pressure—Composition Diagram for the System Nitrogen—Oxygen at 85 °K

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FIGURE 21

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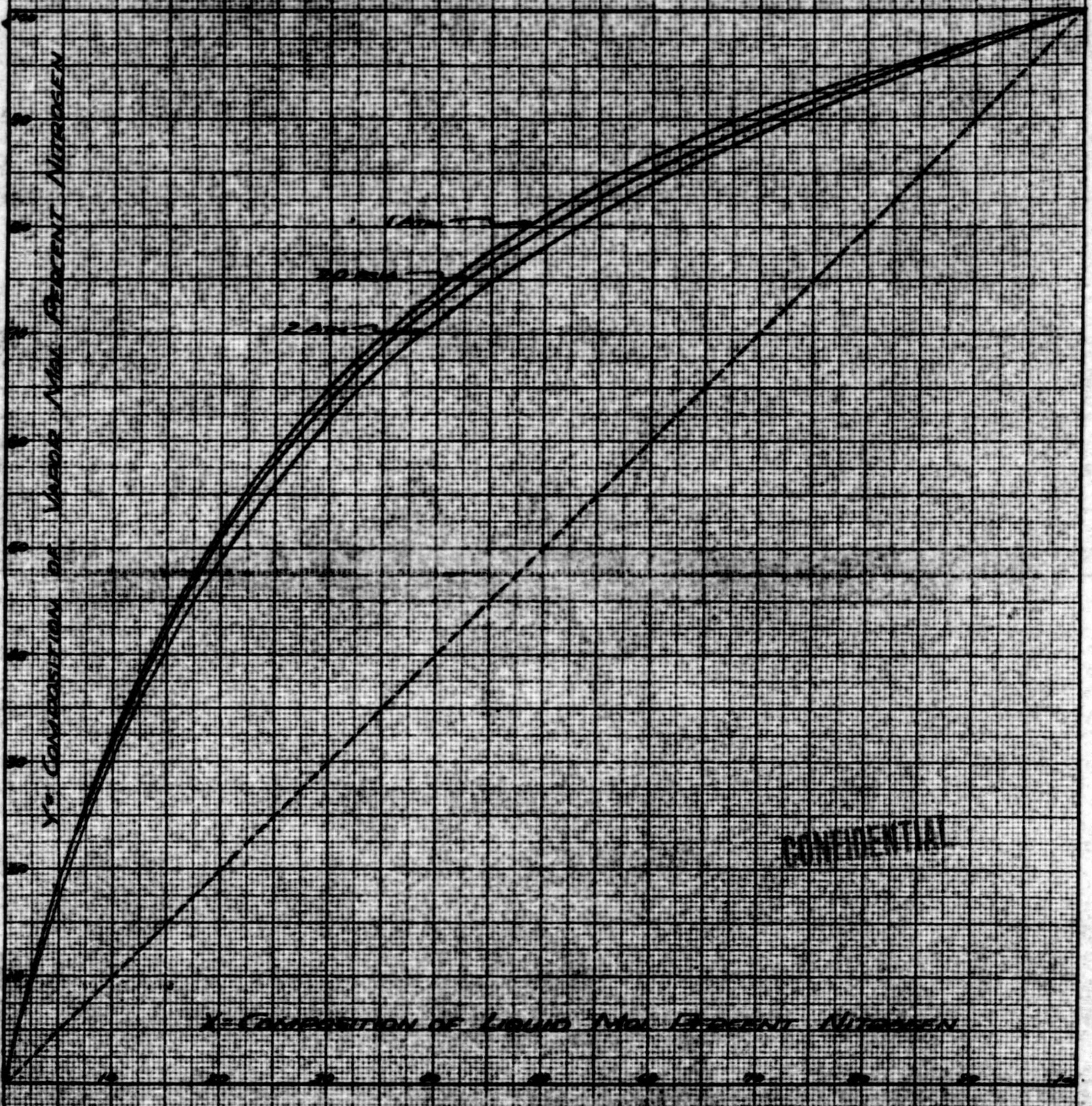
X-Y DIAGRAM FOR THE SYSTEM NITROGEN-OXYGEN



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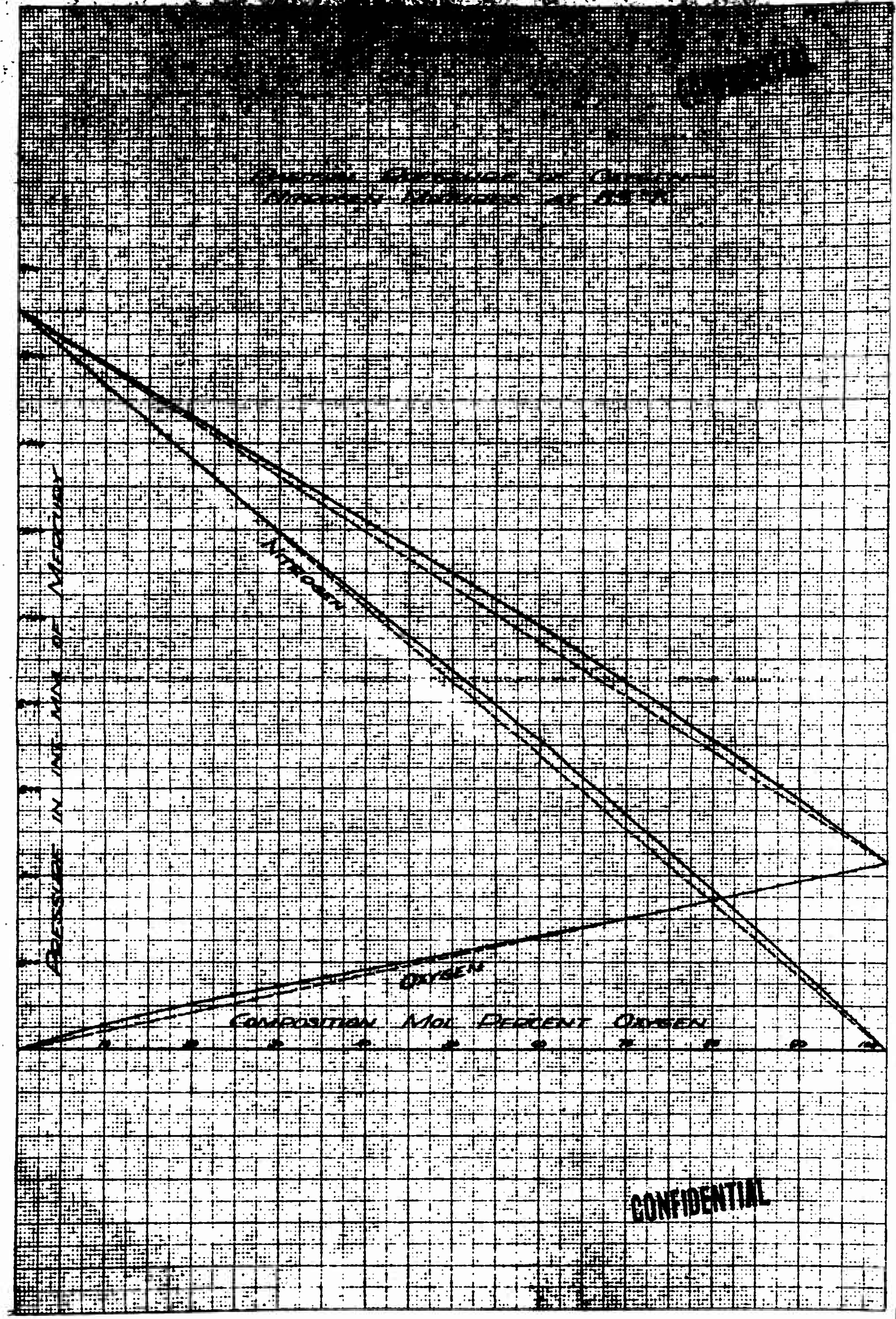

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FIGURE 23

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X-Y DIAGRAM FOR THE SYSTEM
NITROGEN-OXYGEN AT 85°K

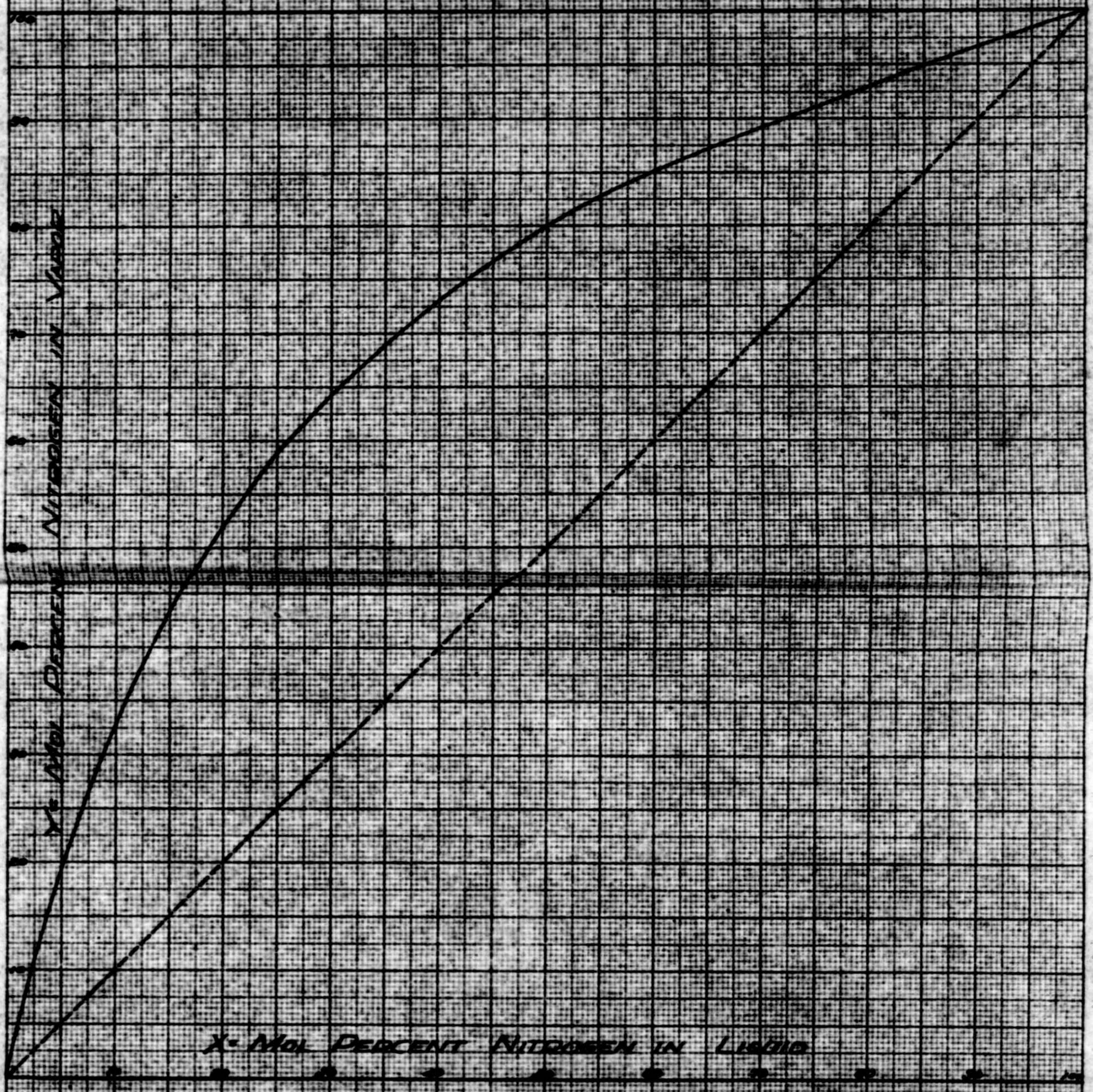

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TABLE XXXI

THE VAPOR PRESSURE OF NITROGEN-OXYGEN MIXTURES BETWEEN 1 AND 2 ATMOSPHERES

$$\text{Log}_{10} P_{atm.} = - A/T + B$$

Mole Percent Oxygen In Liquid	A	B
0	303.28	3.91343
5	303.57	3.90604
10	304.54	3.90046
15	305.86	3.89853
20	307.14	3.89589
25	308.41	3.89238
30	309.64	3.88775
35	310.76	3.88116
40	311.68	3.87033
45	312.54	3.85691
50	312.92	3.84041
55	313.09	3.82034
60	313.52	3.79696
65	314.73	3.77482
70	317.24	3.77799
75	321.21	3.79291
80	326.53	3.81059
85	332.01	3.83546
90	339.06	3.86742
95	349.12	3.92973
100	363.12	4.02571

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TABLE XXXII

BOILING POINT OF NITROGEN-OXYGEN MIXTURES AT 1 AND 2 ATMOSPHERES

Mole Percent O_2 in Liquid	1 Atmosphere Boiling Point °Kelvin	D and D	2 Atmosphere Boiling Point °Kelvin	D and D
0	77.40	(77.33)	83.84	(83.82)
5	77.72		84.21	
10	78.08		84.61	
15	78.46		85.02	
20	78.84	(78.66)	85.44	(85.27)
25	79.23		85.88	
30	79.65		86.33	
35	80.07		86.80	
40	80.52	(80.33)	87.31	(87.14)
45	81.03		87.89	
50	81.48		88.41	
55	81.95		88.96	
60	82.57	(82.54)	89.68	(89.55)
65	83.39		90.62	
70	83.97		91.24	
75	84.69		91.99	
80	85.69	(85.62)	93.04	(92.79)
85	86.61		93.99	
90	87.67		95.07	
95	88.84		96.21	
100	90.20	(90.16)	97.49	(97.43)

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TABLE XXXIII

BOILING POINT OF NITROGEN-OXYGEN MIXTURES AT 20 LBS/SQ. IN. ABS.

Mole Percent Oxygen In Liquid	Boiling Point °Kelvin
0	80.13
5	80.47
10	80.85
15	81.24
20	81.64
25	82,05
30	82.48
35	82.93
40	83.40
45	83.94
50	84.42
55	84.93
60	85.58
65	86.45
70	87.05
75	87.78
80	88.81
85	89.74
90	90.81
95	91.97
100	93,30

TABLE XXXIV

TOTAL PRESSURE ABOVE NITROGEN-OXYGEN MIXTURE AT 85°K.

Mole Percent Oxygen in Liquid	Pressure int. mm.	
0	1703	
5	1642.5	
10	1579.5	
15	1517.0	
20	1456.5	
25	1396.0	
30	1336.0	
35	1276.5	
40	1215.5	
45	1150.5	
50	1096.0	
55	1041.5	
60	975.6	
65	896.0	
70	844.5	
75	784.9	
80	707.7	(706)
85	643.1	
90	574.5	(567)
95	505.0	(498.0)
100	431.0	(426)

The figures in parenthesis are the correct vapor pressures between 80 and 100 percent O_2 in the liquid. The calculated figures are incorrect because the constants in Table XXXI do not extend below 760 mm.

pressure at concentrations that have appeared in plate calculations made on towers tested at the Pennsylvania State College as this was the concentration range liable to be encountered in practice. This would serve as a good check on the value of the equilibrium constants used for the ternary mixtures in the plate calculations mentioned. The results obtained are given in tables XXXV - XXXXV.

Before this work the equilibrium constants at 14.7, 20.0 and 29.4 lbs./sq. in. abs used in the plate calculations were compiled by Mrs. June Pfister from the following binary system data: Nitrogen-oxygen, the data given in this report; Argon-Oxygen, the data given in this report; Argon-Nitrogen, the data of Holst and Hamburger. A complete discussion of these calculations is given in a Formal Report to the N. D. R. C. by Aston and Pfister entitled, "Calculation of the Number of Plates in an Air Rectification Tower."

Figs. 24 - 26 are plots of the data calculated by Aston and Pfister as mentioned above. The points indicated by circles are those determined experimentally on the three component system and listed in tables XXXV - XXXXV. The agreement at 20 lbs./sq. in. abs is not as good as at 14.7 and 29.4 lbs./sq. in. abs due to the uncertainty in the long extrapolation needed. (extrapolation from 22./ to 20.0 lbs./sq. in. abs)

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TABLE XXXV

Run No. 32

Temperature 89.00 °K

Date 12/7/43

Pressure 777.1 mm

System $O_2 - N_2 - A$

Hours for Vaporization 2

Hours Standing 2

Feed Mixture: 0.370434 mols at 84.72% O_2, 10.16% A, 5.12% N_2

Equilibrium Vapor: 0.029074 mols at 71.16% O_2, 13.24% A, 15.60% N_2

Material Balance

	Mols O_2	Mols A	Mols N_2	Total
Feed Mixture	0.313832	0.037636	0.018966	0.370434
Equilibrium Vapor	0.021104	0.003927	0.004626	0.029657
Equilibrium Liquid	0.292728	0.033709	0.014340	0.340777

Equilibrium Liquid: 85.90 % O_2, 9.89 % A, 4.21 % N_2

Equilibrium Vapor Corrected to 760 mm

71.16 % O_2, 13.18 % A, 15.66 % N_2

Equilibrium Temperature Corrected to 760 mm: 88.79 °K

$K_{O_2} = \frac{71.16}{85.90} = 0.8284$, $K_A = \frac{1318}{0.989} = 1.333$, $K_{N_2} = \frac{15.66}{4.21} = 3.720$

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TABLE XXXVI

Run No. 33

Temperature 93.00 °K

Date 12/8/43

Pressure 1148.8 mm

System $O_2 - N_2 - A$

Hours for Vaporization 1.5

Hours Standing 2

Feed Mixture: 0.348090 mols at 85.59 % O_2, 9.96 % A, 4.45 % N_2,

Equilibrium Vapor: 0.031619 mols at 75.01 % O_2, 12.56 % A, 12.43 % N_2

Material Balance

	Mols O_2	Mols A	Mols N_2	Total
Feed Mixture	0.297932	0.034678	0.015480	0.348090
Equilibrium Vapor	0.023717	0.003972	0.003930	0.031619
Equilibrium Liquid	0.274215	0.030706	0.011550	0.316471

Equilibrium Liquid: 86.65 % O_2, 9.70 % A, 3.65 % N_2

Equilibrium Vapor Corrected to 1140 mm

74.96 % O_2, 12.61 % A, 12.43 % N_2

Equilibrium Temperature Corrected to 1140 mm: 92.91 °K

$K_{O_2} = \frac{74.96}{86.65} = 0.8651$, $K_A = \frac{12.61}{9.70} = 1.300$ $K_{N_2} = \frac{12.43}{3.65} = 3.405$

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TABLE XXXVII

Run No. 34

Temperature 36.30 °K

Date 12/9/43

Pressure 1526.4 mm

System $O_2 - N_2 - A$

Hours for Vaporization 1.5

Hours Standing 2

Feed Mixture: 0.326472 mols at 86.29 % O_2, 9.79 % A, 3.92 % N_2

Equilibrium Vapor: 0.040949 mols at 78.18 % O_2, 12.12 % A, 9.70 % N_2

Material Blance

	Mols O_2	Mols A	Mols N_2	Total
Feed Mixture	0.281716	0.031963	0.012793	0.326472
Equilibrium Vapor	0.032014	0.004963	0.003972	0.040949
Equilibrium Liquid	0.249702	0.027000	0.008821	0.285523

Equilibrium Liquid: 87.45 % O_2, 9.46 % A, 3.09 % N_2

Equilibrium Vapor Corrected to 1520 mm

78.16 % O_2, 12.13 % A, 9.71 % N_2

Equilibrium Temperature Corrected to 1520 mm: 96.25 °K

$$K_{O_2} = \frac{78.16}{87.45} = 0.8938,\quad K_A = \frac{12.13}{9.46} = 1.282,\quad K_{N_2} = \frac{9.71}{3.09} = 3.142$$

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TABLE XXXVIII

Run No. 35

Temperature 89.39 °K

Date 12/11/43

Pressure 782.9 mm

System O_2 - N_2 - A

Hours for Vaporization 2

Hours Standing 2.5

Feed Mixture: 0.298723 mols at 87.05% O_2, 9.57% A, 3.38% N_2

Equilibrium Vapor: 0.029830 mols at 77.13% O_2, 12.74% A, 10.13% N_2

Material Balance

	Mols O_2	Mols A	Mols N_2	Total
Feed Mixture	0.260022	0.028600	0.010101	0.298723
Equilibrium Vapor	0.023008	0.003800	0.003022	0.029830
Equilibrium Liquid	0.237014	0.024800	0.007079	0.268893

Equilibrium Liquid: 88.15 % O_2, 9.22 % A, 2.63 % N_2

Equilibrium Vapor Corrected to 760 mm

77.04 % O_2, 12.79 % A, 10.17 % N_2

Equilibrium Temperature Corrected to 760 mm: 89.10 °K

$$K_{O_2} = \frac{77.04}{88.15} = \underline{0.8740},\quad K_A = \frac{12.79}{9.22} = \underline{1.387},\quad K_{N_2} = \frac{10.17}{2.63} = \underline{3.867}$$

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TABLE XXXIX

Run No. 36

Temperature 88.73 °K

DATE 12/15/43

Pressure 756.05 mm

SYSTEM $O_2 - N_2 - A$

Hours for Vaporization 1.5

Hours Standing 2

Feed Mixture: 0.404078 mols at 89.30% O_2, 5.23% A, 5.47% N_2

Equilibrium Vapor: 0.028659 mols at 76.57% O_2, 6.62 % A, 16.81 % N_2

Material Balance

	Mols O_2	Mols A	Mols N_2	Total
Feed Mixture	0.360842	0.021133	0.022103	0.404078
Equilibrium Vapor	0.021944	0.001897	0.004818	0.028659
Equilibrium Liquid	0.338898	0.019236	0.017285	0.375419

Equilibrium Liquid: 90.27 % O_2, 5.12 % A, 4.61 % N_2

Equilibrium Vapor Corrected to 760 mm

76.57 % O_2, 6.63 % A, 16.80 % N_2

Equilibrium Temperature Corrected to 760 mm: 88.78 °K

$$K_{O_2} = \frac{76.57}{90.27} = 0.8482, \quad K_A = \frac{6.63}{5.12} = 1.295, \quad K_{N_2} = \frac{16.80}{4.61} = 3.644$$

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TABLE XL

Run no. 37

Temperature 92.66 °K

Date 12/16/43

Pressure 1098.1 mm

System $O_2 - N_2 - A$

Hours for Vaporization 1.5

Hours Standing 2

Feed Mixture: 0.382135 mols at 90.03 % O_2, 5.15 % A, 4.82 % N_2

Equilibrium Vapor: 0.033357 mols at 79.41 % O_2, 6.58 % A, 14.01 % N_2

Material Balance

	Mols O_2	Mols A	Mols N_2	Total
Feed Mixture	0.344086	0.019684	0.018425	0.382195
Equilibrium Vapor	0.026886	0.002228	0.004743	0.033857
Equilibrium Liquid	0.317200	0.017456	0.013682	0.348338

Equilibrium Liquid: 91.06 % O_2, 5.01 % A, 3.93 % N_2

Equilibrium Vapor Corrected to 1140 mm

79.57 % O_2, 6.53 % A, 13.90 % N_2

Equilibrium Temperature Corrected to 1140 mm: 92.90 °K

$K_{O_2} = \frac{79.57}{91.06} = 0.8738$, $K_A = \frac{6.53}{5.01} = 1.303$, $K_{N_2} = \frac{13.90}{3.93} = 3.537$

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TABLE XLI

Run No. 38

Temperature 96.41 °K

Date 12/16/43

Pressure 1512.3 mm

System O_2-N_2-A

Hours for Vaporization 1.5

Hours Standing 2.5

Feed Mixture: 0.357834 mols at 90.75% O_2, 5.05 % A, 4.20 % N_2

Equilibrium Vapor: 0.038994 mols at 82.31% O_2, 6.49 % A, 11.20% N_2

Material Balance

	Mols O_2	Mols A	Mols N_2	Total
Feed Mixture	0.324741	0.018081	0.015012	0.357834
Equilibrium Vapor	0.032096	0.002531	0.004367	0.038994
Equilibrium Liquid	0.292645	0.015550	0.010645	0.318840

Equilibrium Liquid: 91.78 % O_2, 4.88 % A, 3.34 % N_2

Equilibrium Vapor Corrected to 1520 mm

82.34 % O_2, 6.46 % A, 11.20 % N_2

Equilibrium Temperature Corrected to 1520 mm: 96.47 °K

$$K_{O_2} = \frac{82.34}{91.78} = 0.8971, \quad K_A = \frac{6.46}{4.88} = 1.324, \quad K_{N_2} = \frac{11.20}{3.34} = 3.353$$

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TABLE XLII

Run No. 39

Temperature 88.96 °K

Date 12/21/43

Pressure 735.45 mm

System O_2-N_2-A

Hours for Vaporization 1.5

Hours Standing 2.0

Feed Mixture: 0.331541 mols at 91.42 % O_2, 4.94 % A, 3.64 % N_2

Equilibrium Vapor: 0.027788 mols at 82.83 % O_2, 6.53 % A, 10.64 % N_2

Material Balance

	Mols O_2	Mols A	Mols N_2	Total
Feed Mixture	0.303099	0.016375	0.012067	0.331541
Equilibrium Vapor	0.023016	0.001815	0.002957	0.027788
Equilibrium Liquid	0.280083	0.014560	0.009110	0.303753

Equilibrium Liquid: 92.21 % O_2, 4.79 % A, 3.00 % N_2

Equilibrium Vapor Corrected to 760 mm

82.93 % O_2, 6.48 % A, 10.59 % N_2

Equilibrium Temperature Corrected to 760 mm: 89.28 °K

$$K_{O_2} = \frac{82.93}{92.21} = 0.8994, \quad K_A = \frac{6.48}{4.79} = 1.353, \quad K_{N_2} = \frac{10.59}{3.00} = 3.530$$

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TABLE XLIII

Run No. 40

Temperature 85.54 °K

Date 12/27/43

Pressure 768.7 mm

System O_2-N_2-A

Hours for Vaporization 1.5

Hours Standing 2.5

Feed Mixture: 0.399484 mols at 65.98% O_2, 8.93 % A, 25.09% N_2

Equilibrium Vapor: 0.028948 mols at 41.33% O_2, 8.03 % A, 50.64% N_2

Material Balance

	Mols O_2	Mols A	Mols N_2	Total
Feed Mixture	0.263580	0.035674	0.100230	0.399484
Equilibrium Vapor	0.011964	0.002325	0.014659	0.028948
Equilibrium Liquid	0.251616	0.033349	0.085571	0.370536

Equilibrium Liquid: 67.91 % O_2, 9.00 % A, 23.09 % N_2

Equilibrium Vapor Corrected to 760 mm

41.28 % O_2, 8.04 % A, 50.68 % N_2

Equilibrium Temperature Corrected to 760 mm: 85.43 °K

$$K_{O_2} = \frac{41.28}{67.91} = 0.6079,\quad K_A = \frac{8.04}{9.00} = 0.8933,\quad K_{N_2} = \frac{50.68}{23.09} = 2.195$$

TABLE XLIV

Run No. 41

Temperature 81.31 °K

Date 12/28/43

Pressure 768.4 mm

System O_2-N_2-A

Hours for Vaporization 1.5

Hours Standing 2.0

Feed Mixture: 0.382650 mols at 41.79% O_2, 4.55 % A, 53.66% N_2

Equilibrium Vapor: 0.029051 mols at 16.80% O_2, 2.43 % A, 80.77% N_2

Material Balance

	Mols O_2	Mols A	Mols N_2	Total
Feed Mixture	0.159909	0.017411	0.205330	0.382650
Equilibrium Vapor	0.004915	0.000590	0.023546	0.029051
Equilibrium Liquid	0.154994	0.016821	0.181784	0.353599

Equilibrium Liquid: 43.83 % O_2, 4.76 % A, 51.41 % N_2

Equilibrium Vapor Corrected to 760 mm

16.75 % O_2, 2.54 % A, 80.71 % N_2

Equilibrium Temperature Corrected to 760 mm: 81.20 °K

$$K_{O_2} = \frac{16.75}{43.83} = 0.3822, \quad K_A = \frac{2.54}{4.76} = 0.5336, \quad K_{N_2} = \frac{81.20}{51.41} = 1.574$$

TABLE XLV

Run No. 42

Temperature 85.30 °K

Date 1/6/44

Pressure 1129.1 mm

System O_2-N_2-A

Hours for Vaporization 1.5

Hours Standing 2.5

Feed Mixture: 0.360782 mols at 43.30% O_2, 4.70 % A, 52.00 % N_2

Equilibrium Vapor: 0.035834 mols at 17.13% O_2, 2.70 % A, 80.17% N_2

Material Balance

	Mols O_2	Mols A	Mols N_2	Total
Feed Mixture	0.156209	0.016967	0.187606	0.360782
Equilibrium Vapor	0.006138	0.000968	0.028728	0.035834
Equilibrium Liquid	0.150071	0.015999	0.158878	0.324948

Equilibrium Liquid: 46.18 % O_2, 4.93 % A, 48.89 % N_2

Equilibrium Vapor Corrected to 1140 mm

17.16 % O_2, 2.72 % A, 80.12 % N_2

Equilibrium Temperature Corrected to 1140 mm: 85.40 °K

$$K_{O_2} = \frac{17.16}{46.18} = 0.3716,\quad K_A = \frac{2.72}{4.93} = 0.5517,\quad K_{N_2} = \frac{80.12}{48.89} = 1.639$$

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TABLE XLVI

Run No. 43

Temperature 85.09 °K

Date 3/31/44

Pressure 801.99 mm

System A-O_2-N_2

Hours for Vaporization 1.25

Hours Standing 2

Feed Mixture: 0.369297 mols at 63.47 %O_2, 9.78 %A, 26.75 %N_2

Equilibrium Vapor: .030032 mols at 37.82 %O_2, 8.26 %A, 53.92 %N_2

Material Balance

	Mols O	Mols A	Mols N	Total
Feed Mixture	0.234393	0.036117	0.098787	0.369297
Equilibrium Vapor	0.011358	0.002481	0.016193	0.030032
Equilibrium Liquid	0.223035	0.033636	0.082594	0.339265

Equilibrium Liquid: 65.74 %O_2, 9.91 %A, 24.35 %N_2

Equilibrium Vapor Corrected to 760 mm

37.68 %O_2, 8.08 %A, 54.24 %N_2

Equilibrium Temperature Corrected to 760 mm: 84.60 °K

$K_{O_2} = \frac{37.68}{65.74} = 0.5732$, $K_A = \frac{8.08}{9.91} = 0.8153$, $K_{N_2} = \frac{54.24}{24.35} = 2.228$

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TABLE XLVII

Run No. 44

Temperature 88.22 °K

Date 5/1/44

Pressure 1055.3 mm

System A - O_2 - N_2

Hours for Vaporization 1.5

Hours Standing 1.5

Feed Mixture: 0.345864 mols at 65.21 %O_2, 9.88 %A, 24.91 %N_2

Equilibrium Vapor: 0.033631 mols at 40.11 %O_2, 8.41 %A, 51.48 %N_2

Material Balance

	Mols O_2	Mols A	Mols N_2	Total
Feed Mixture	0.225531	0.034181	0.086152	0.345864
Equilibrium Vapor	0.013489	0.002828	0.017314	0.033631
Equilibrium Liquid	0.212042	0.031353	0.068838	0.312233

Equilibrium Liquid: 67.91 %O_2, 10.04 %A, 22.05 %N_2

Equilibrium Vapor Corrected to 1034 mm

40.10 %O_2, 8.24 %A, 51.66 %N_2

Equilibrium Temperature Corrected to 1034 mm: 88.03 °K

$$K_{O_2} = \frac{40.10}{67.91} = .5905, \quad K_A = \frac{8.24}{10.04} = .8207, \quad K_{N_2} = \frac{51.66}{22.05} = 2.343$$

TABLE XLVIII

Run No. 45

Temperature 93.77 °K

Date 4/3/44

Pressure 1583.8 mm

System A - O_2 - N_2

Hours for Vaporization 1.5

Hours Standing 1.5

Feed Mixture: 0.320847 mols at 67.16 % O_2, 10.00 % A, 22.84 % N_2

Equilibrium Vapor: 0.043702 mols at 45.38 % O_2, 9.68 % A, 44.94 % N_2

Material Balance

	Mols O_2	Mols A	Mols N_2	Total
Feed Mixture	0.215497	0.032077	0.073273	0.320847
Equilibrium Vapor	0.019832	0.004230	0.019640	0.043702
Equilibrium Liquid	0.195665	0.027847	0.053633	0.277145

Equilibrium Liquid: 70.60 % O_2, 10.05 % A, 19.35 % N_2

Equilibrium Vapor Corrected to 1520 mm

45.49 % O_2, 9.15 % A, 45.36 % N_2

Equilibrium Temperature Corrected to 1520 mm: 93.37 °K

$$K_{O_2} = \frac{45.49}{70.60} = 0.6443, \quad K_A = \frac{9.15}{10.05} = 0.9104, \quad K_{N_2} = \frac{45.36}{19.35} = 2.344$$

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TABLE XLIX

Run No. 48

Temperature 88.91 °K

Date 4/27/44

Pressure 1576.2 mm

System $A - O_2 - N_2$

Hours for Vaporization 1.5

Hours Standing 1.5

Feed Mixture: 0.322332 mols at 41.28 $\%O_2$, 5.07 %A, 53.65 $\%N_2$

Equilibrium Vapor: 0.054745 mols at 19.85 $\%O_2$, 3.33 %A, 76.82 $\%N_2$

Material Balance

	Mols O_2	Mols A	Mols N_2	Total
Feed Mixture	0.133044	0.016348	0.172940	0.322332
Equilibrium Vapor	0.010867	0.001823	0.042055	0.054745
Equilibrium Liquid	0.122177	0.014525	0.130885	0.267587

Equilibrium Liquid: 45.66 $\%O_2$, 5.43 %A, 48.91 $\%N_2$

Equilibrium Vapor Corrected to 1520 mm

19.61 $\%O_2$, 3.31 %A, 77.08 $\%N_2$

Equilibrium Temperature Corrected to 1520 mm: 88.46 °K

$$K_{O_2} = \frac{19.61}{45.66} = .4295, \quad K_A = \frac{3.31}{5.43} = .6096, \quad K_{N_2} = \frac{77.08}{48.91} = 1.576$$

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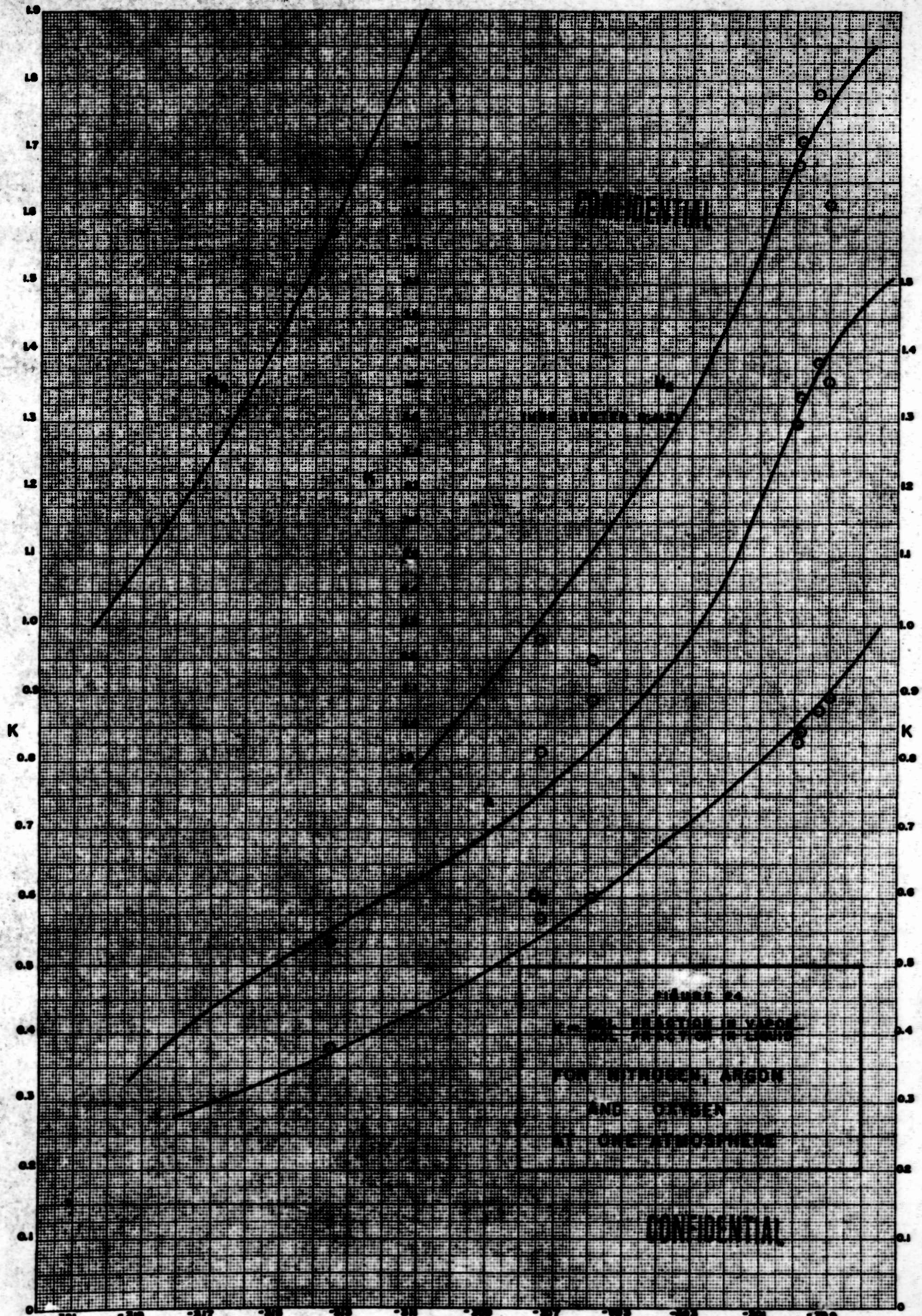

FIGURE 24

$K = \frac{\text{MOL FRACTION IN VAPOR}}{\text{MOL FRACTION IN LIQUID}}$

FOR NITROGEN, ARGON AND OXYGEN AT ONE ATMOSPHERE

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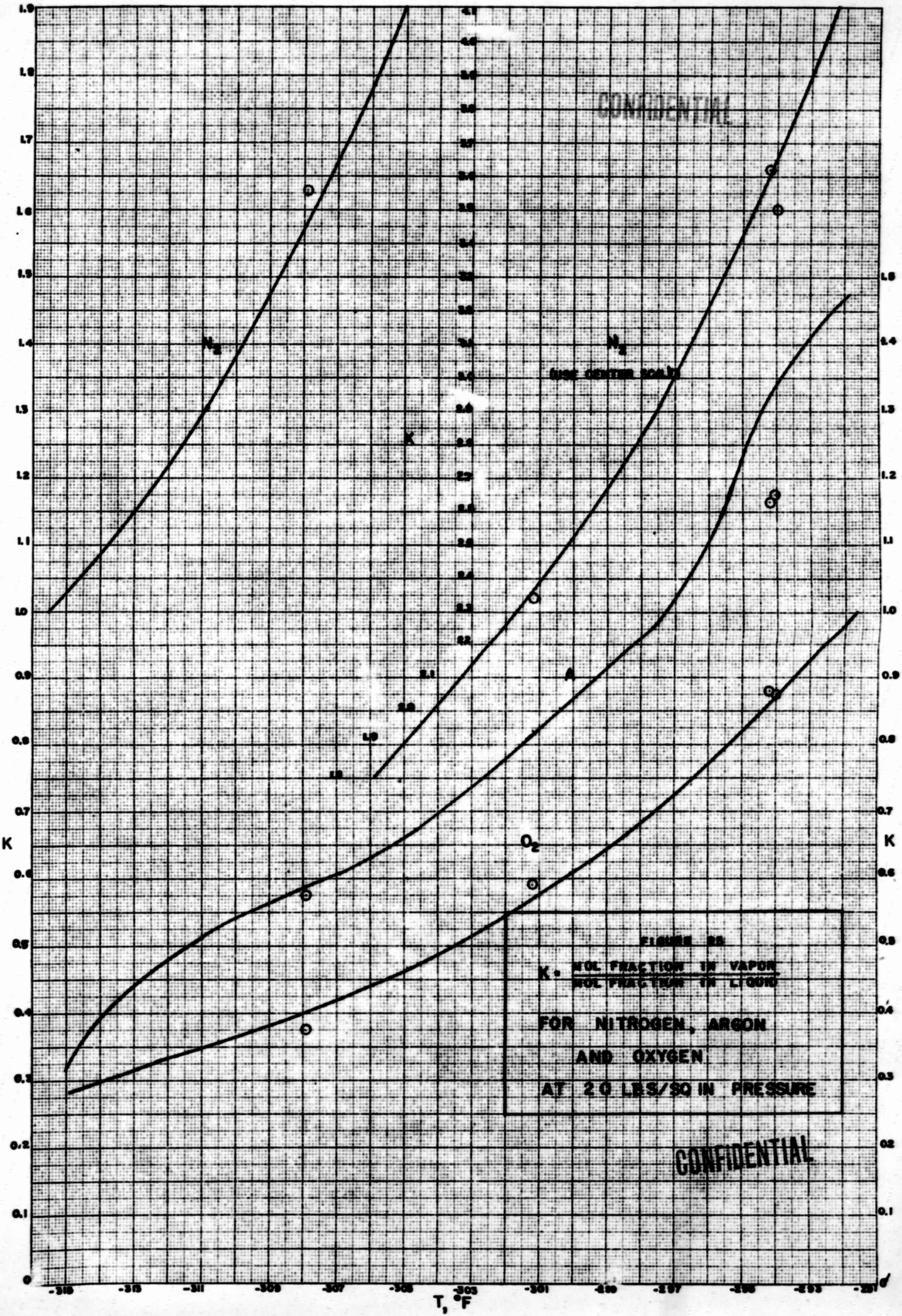

FIGURE 25

$K = \frac{\text{MOL FRACTION IN VAPOR}}{\text{MOL FRACTION IN LIQUID}}$

FOR NITROGEN, ARGON
AND OXYGEN
AT 20 LBS/SQ IN PRESSURE

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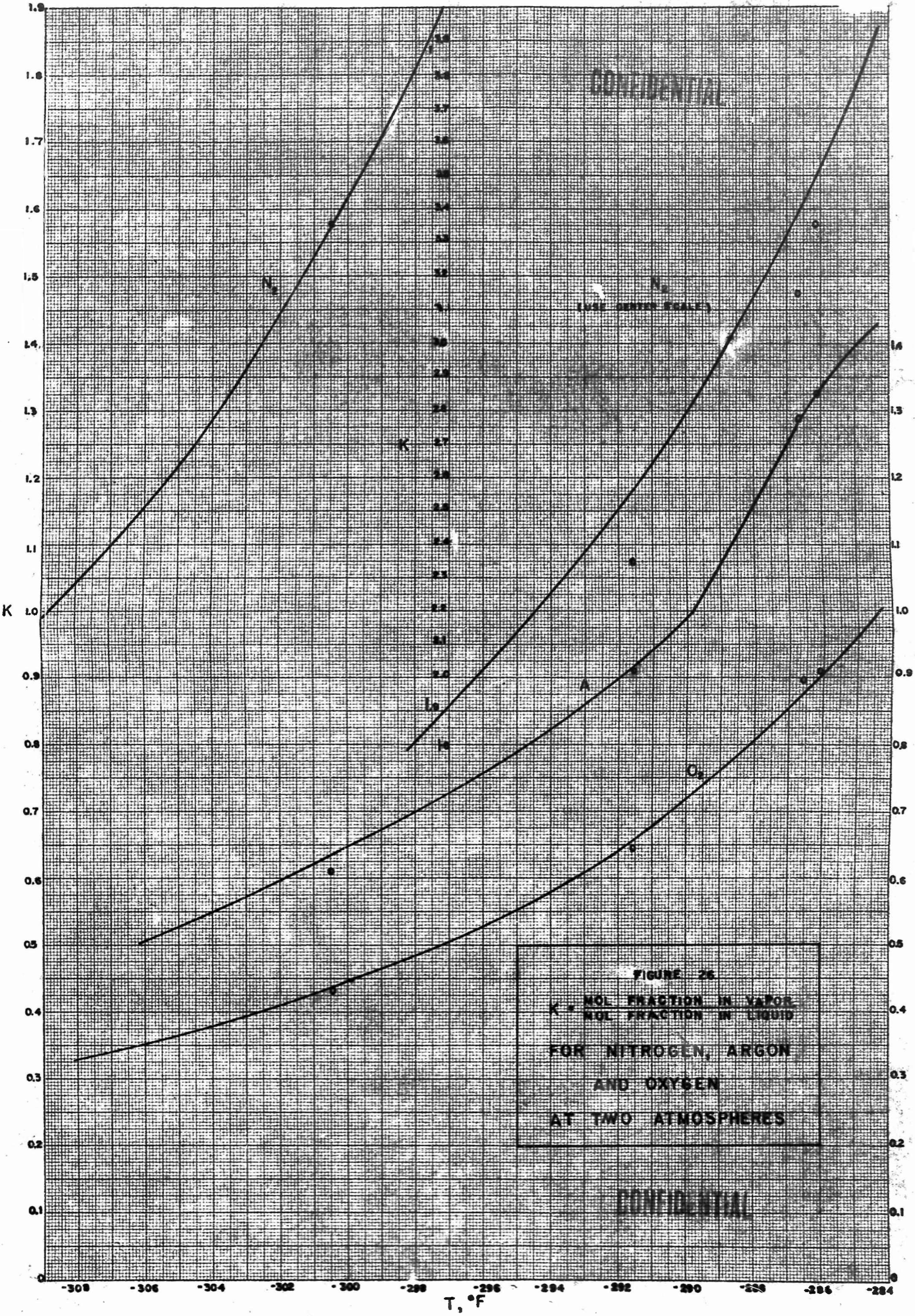

FIGURE 26

$K = \frac{\text{MOL FRACTION IN VAPOR}}{\text{MOL FRACTION IN LIQUID}}$

FOR NITROGEN, ARGON AND OXYGEN AT TWO ATMOSPHERES

REFERENCES:

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APPENDIX

Comparison of Equilibrium Measurements Obtained in the Two Different Apparati

Three equilibrium determinations were made on the argon-oxygen system at one atmosphere pressure in the new equilibrium apparatus described on page 24. These were to be used to compare with the data obtained in calorimeter "C", page 10, and thereby test the approach to equilibrium in the old apparatus since equilibrium in the new apparatus is established much more rapidly.

The three equilibrium constants obtained are listed in table I. Column one lists the mole percent argon in the liquid. Column two lists the experimental equilibrium constant for argon determined in the new apparatus. Column three lists the equilibrium constant for argon, corresponding to the concentration of column one, from the data obtained in calorimeter "C". These values were interpolated from figure 9, page 16a. Column four lists the percent deviation of the two determinations.

The good agreement between the two sets of data shows the consistency of the data obtained in the two apparati.

TABLE L

COMPARISON OF EQUILIBRIUM MEASUREMENTS OBTAINED IN THE TWO DIFFERENT APPARATI

Mole Percent Argon in Liquid	K = y/x new Apparatus	K = y/x Calorimeter C	Percent Deviation
4.99	1.475	1.478	0.20
17.69	1.395	1.402	0.36
23.77	1.372	1.362	0.58

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TITLE: Final Report on Vapor - Liquid Equilibrium for the System Oxygen-Nitrogen-Argon

AUTHOR(S): Sagenkahn, Malcom L.; Fink, Herman L.; Aston, J. G.
ORIGINATING AGENCY: Pennsylvania State College, State College, Pa.
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ABSTRACT:

The investigation of the vapor-liquid equilibrium for the system oxygen-nitrogen-argon has been completed, and the work accomplished on the various phases of this study has been summarized. All the available equilibrium data for the two component systems of oxygen-nitrogen-argon mixtures were summarized and tested for their reliability, by means of the Duhem equation. The apparatus and Method used for measurements of the liquid-vapor equilibria in the system oxygen-argon are described, as well as an apparatus for obtaining liquid-vapor equilibria by a static method which comes to equilibrium rapidly. An analytical procedure for determining compositions of oxygen-nitrogen-argon mixtures was developed. Data for the systems argon-oxygen and oxygen-nitrogen-argon to two atmospheres of pressure were obtained.

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P7/4

* Phase transformations
Chemical equilibrium
Gas Dynamics

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TITLE: Vapor-Liquid Equilibrium for the System Oxygen-Nitrogen-Argon

AUTHOR(S): Aston, J. G.
ORIGINATING AGENCY: Pennsylvania State College
PUBLISHED BY: Office of Scientific Research and Development, NDRC, Div 11

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ABSTRACT:

All the available equilibrium data for the two component system of oxygen-nitrogen-argon mixtures have been summarized, and they have been tested for their reliability by means of the Duhem equation. The apparatus and method used for measurements of the liquid-vapor equilibria in the system oxygen-argon are described. Complete vapor-liquid equilibrium data for the system argon-oxygen at one atmosphere pressure over the entire range of composition have been obtained. Vapor pressures for argon-oxygen mixtures over the entire composition range and at pressures ranging from 550 to 850 mm of Hg have been determined and equations calculated for them. An analytical procedure for determining compositions of oxygen-nitrogen-argon mixtures has been developed. Data for the systems argon-oxygen, nitrogen-oxygen, and oxygen-nitrogen-argon at two atmospheres pressure have been obtained using a new equilibrium apparatus.

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(4)
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(10
2)

SUBJECT HEADINGS: Gas mixtures - Equilibrium composition (44034)

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