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# Progress Report on "Vapor-Liquid Equilibrium Data for the System Argon-Oxygen"

to
May 15, 1943
by
J. G. Aston, S. C. Schumann, H. L. Fink, M. L. Sagenkahn, W. W. Bodle

Report OSRD No. 1581

Copy No. 32

Date: July 9, 1943

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NATIONAL DEFENSE Research Committee

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OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

Section 11.1

# Progress Report on "Vapor-Liquid Equilibrium Data for the System Argon-Oxygen"

Service Directive NLB-6d

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Forwarding report and noting:

> "This report augments information presented in OSRD No. 1507 of importance to the design of equipment for the rectification of air."

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

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Final Report on

# VAPOR - LIQUID EQUILIBRIUM DATA FOR THE SYSTEM ARGON - OXYGEN OVER THE ENTIRE RANGE OF COMPOSITION

by

J. G. Aston, S. C. Schumann, H. L. Fink, M. L. Sagenkahn
and W. N. Bodle.

May 15, 1943

Submitted by J. G. Aston
Official Investigator, N.D.R.C.

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## SUMMARY

1. The vapor pressure of certain liquid mixtures of argon and oxygen has been measured and the results expressed by simple equations.
2. From the data normal boiling points of the liquid mixtures were computed as well as total pressures at 88.5°K.
3. Compositions of the vapor and liquid in equilibrium have been measured at approximately one atmosphere total pressure over a wide range of concentration and "K values" compiled from the results.
4. The composition of the vapor in equilibrium with the liquid has been computed at 88.5°K. over a wide range of composition.
5. The partial pressures of argon and oxygen over a wide range of liquid composition at 88.5°K. have been found in accord with the Duhem equation.
6. The Duhem equation has been used to check the data on the oxygen-nitrogen system.

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## VAPOR-LIQUID EQUILIBRIUM DATA FOR THE SYSTEM AGRON-OXYGEN OVER THE ENTIRE RANGE OF COMPOSITION

Data on the vapor-liquid equilibrium for the system argon-oxygen are essential for calculations of the distribution of argon, oxygen and nitrogen throughout air rectification columns. This report presents experimental data taken on this sytem over the last year.

Bourbo and Ishkin[1] obtained similar results of less accuracy from a study of the equilibrium pressures alone and therefore used the equation

$$dy_1 = \frac{y_1(1-y_1)}{P(y_1-x_1)} \, dP \qquad \ldots\ldots\ldots\ldots\ldots (1)$$

where

$y_1$ is the mole fraction of argon in the vapor phase

$x_1$ is the mole fraction of argon in the liquid phase

P is the total pressure.

The vapor-liquid equilibrium concentrations were obtained by determining total pressures for the total range of concentrations at three temperatures. The integration was accomplished using the general method of Runge[2]. The only assumption involved in equation (1) is the perfection of the gaseous state.

In addition to these data an unpublished experimental determination of the equilibrium has been made by Schilling[3]. He has kindly made this data available to us. The lowest concentration studied was 6% argon[4].

---

(1) Bourbo and Ishkin, Phys. Zeitschr. d. Sowjetunion 10, 271 (1936).
(2) Kritschewski and Kozarnowski, Z. Anorg. Allgem. Chem. 218, 49 (1934).
(3) C. Schilling, unpublished work.
(4) In all subsequent description concentrations will be expressed in mole per cent argon, unless otherwise stated.

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**Apparatus:**

The laboratory isothermal calorimeter, C, was used for these measurements[5]. 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 1. 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 Goloz 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.

Both the three liter and the 0.2 liter calibrated bulbs could be filled with mercury from the reservoirs beneath them without contamination.

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(5) Aston and Messerly, J. Am. Chem. Soc. 58, 2354 (1936).
Messerly and Aston, ibid. 62, 886 (1940).

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By means of a bicycle pump or a vacuum pump, pressure or vacuum could be applied on 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[6]. 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 traces 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 to glass 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.

---

(6) Von Siemens, Ann. Physik., 42, 871 (1913).

**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 0.008 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 now 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.
$y'_1$ = moles of argon gas remaining in the calorimeter system.
$y'_2$ = 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

$$x_1 = n_1 - (y_1 + y_1') \qquad (2)$$

$$x_2 = n_2 - (y_2 + y_2') \qquad (3)$$

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 $y_1'$ is calculated from

$$y_1' = \left(\frac{y_1}{y_1+y_2}\right) \frac{P \sum v/T}{R} \, ; \qquad (4)$$

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 (4) exists for $y'_2$.

For the next vaporization, the moles of argon and oxygen originally in the calorimeter system are $(x_1 + y_1')$ and $(x_2 + y'_2)$ 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% and 100% $O_2$, the method used was that of Badger[7] 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 per cent. Analysis of the pure oxygen produced from $KMnO_4$ gave estimated results of 99.99%, 99.99% and 100.01% for three analyses.

---

(7) Badger. Ind. Eng. Chem. 12, 161 (1920).

For analysis of mixtures containing from 0-97% oxygen, a conventional Orsat procedure was employed using the commercial absorbent [illegible][8]. This absorbent was the most rapid and accurate absorbent of those tried; it behaved very similarly to Fieser's solution[9]. A three foot water jacketed burette was used for these analyses. Readings on this burette could be estimated to 0.03 per cent but the accuracy of determination is probably from 0.05 to 0.10 per cent. In these analyses, the apparatus was checked before each series by analysis for $O_2$ in air.

The method of transfer of the gas to be analysed to the burette involved no intermediate containing vessels. The sample was drawn into the burette, through 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 vapor was always high in argon content. With the method used of filling the calorimeter, the gas phase originally consisted of 100% argon. It is demonstrated presently that the time to reach equilibrium for this is too long to be practical[10]. Therefore, the results of this first vaporization were discarded in all series.

---

(8) Furnished by the Hays Corporation, Michigan City, Indiana.
(9) Fieser. J. Am. Chem. Soc. 46, 2639 (1924).
(10) Only one vapor produced from the first vaporization ever reached complete equilibrium. After seventy-two hours analysis showed the mixture to be at equilibrium. This data was used in a later calculation as will be seen.

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 (4). 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 not 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 V.

<u>Temperature Scale</u>:

The temperature scale of The Pennsylvania State College Cryogenic Laboratory was employed with 0°C. equal to 273.16°K. This scale has been retained in terms of hydrogen and oxygen vapor pressures. The indication of S-4 and S-7 were corrected according to a comparison with oxygen vapor pressures in October, 1941 which were given the values determined on our temperature scale in 1935.

<u>Vapor Pressures</u>:

The total pressure above mixtures from 0 - 87% argon was measured as described above. The values are given in Table I. The observed pressure in international millimeters and temperature in degrees Kelvin as read on R-100 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 I indicate that the 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 II, where column one gives the composition in mole per cent 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 I. 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 87.30 ± .05°K. (-185.86°C.). Values for the normal boiling point of argon reported in the literature are those of Ramsay and Travers (-186.1°C.)[11], Crommelin (-185.84°C.)[12], Mathias, Onnes and Crommelin (-185.66°C.)[13] and Bourbo and Ishkin (-185.9°C.)[14]. 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[15], viz, 90.19 based upon a critical study of the literature.

---

(11) Ramsay and Travers, Z. Phys. Chem. 38, 686 (1901).
(12) Crommelin, Comm. Phys. Lab. Leiden No. 138C (1913).
(13) Mathias, Onnes and Crommelin, ibid. No. 131a (1913).
(14) Bourbo and Ishkin, Phys. Zeitschr. d. Sowjetunion 10,271 (1936).
(15) Hoge and Brickwedde, Temperature. It's Measurements and Control in Science and Industry. American Institute of Physics, Reinhold Publishing Corp. (1941).

Table III 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 II, represent the boiling curve at this pressure.

Table IV lists the total pressure for various mixtures at a temperature at 88.57°K. as obtained from Table II.

**Equilibrium Data:**

Table V 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 II shows this plot on a smaller scale. For convenience the smoothed values of $y/x$ are listed in Table VI.

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 per cent of gas in equilibrium with liquid of a specific concentration may be in error by 0.03 mole per cent for low argon concentrations and by 0.15 mole per cent for high argon concentrations. The third column of Table VI lists the percentage error in $y/x$ on this basis.

The conventionally represented T, X diagram, summarizing all the data is shown in Figure III. The low volatility of argon at high concentrations found by Schilling and by Bourbo and Ishkin has been substantiated. Figure IV is a more detailed plot of argon-oxygen liquid-vapor equilibrium, 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 pressure 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 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 -

$$P_1 = P_1^0 \, a_1 \qquad (5)$$

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

$$P_1 \, (88.57°K.) = P_1 \, (T) \, \frac{P_1^0 \, (88.57°K.)}{P_1^0 \, (T)} \qquad (6)$$

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.

$P_1^0$(88.57°K.) is the vapor pressure of pure liquid argon at 88.57°K.

$P_1^0$(T) is the vapor pressure of pure liquid argon at T.

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

Likewise, the similar equation -

$$P_2 \, (88.57°K.) = P_2(T) \, \frac{P_2^0(88.57°K.)}{P_2^0(T)} \qquad (7)$$

relates the partial pressure of oxygen at 88.57 to the partial pressures experimentally obtained at 760 mm.[15]. Table VII summarizes the results over the complete concentration range. It is seen that the results obtained at 88.57°K. differ from those obtained at 760 int. mm. by only 0.9 per cent at the greatest. Figure V 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 VI. In Figure VII 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.

In Table VIII the data of this research are compared with that of Bourbo and Ishkin, and that of Schilling. Although the data of both are given at different temperatures, and at different temperatures 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

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(15) An equation similar to (6), which however allows for the change in the activity of the pure components with temperature is:

$$P_1(88.57°K.) = P_1(T)\ \frac{\left[P_1(88.57)+P_2(88.57)\right]\left[P_1^\circ(88.57)\right]\left[N_1P_1^\circ(T)+N_2P_2^\circ(T)\right]}{\left[P_1(T)+P_2(T)\right]\left[N_1P_1^\circ(88.57)+N_2P_2^\circ(88.57)\right]\left[P_1^\circ(T)\right]} \qquad (8)$$

and gives results almost identical with equation (6). The use of equation (8) 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.

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 phase at a particular point to the liquid phase is represented by

$$A_l \underset{k_2}{\overset{k_1}{\rightleftarrows}} A_g \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

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 -

$$\frac{d\,A_g}{dt} = k_1 A_l - k_2 A_g \quad \ldots\ldots\ldots\ldots \quad (10)$$

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

$$k_2 A_g = k_1 A_l \quad \ldots\ldots\ldots\ldots\ldots \quad (11)$$

or

$$\frac{A_g}{A_l} = \frac{k_1}{k_2} = K \quad \ldots\ldots\ldots\ldots \quad (12)$$

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

$$n_g A_g + n_l A_l = n_A \qquad (13)$$

where $n_g$ = the total moles of gas
$n_l$ = the total moles of liquid
$n_A$ = the total moles of argon

Substituting (12) and (13) in (10)

$$\frac{d A_g}{\frac{K n_A}{n_l} - A_g\left(\frac{K n_g}{n_l} + 1\right)} = k_2 \, dt \qquad (14)$$

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

$$\frac{1}{\left(\frac{K n_g}{n_l} + 1\right)} \log \frac{\left[\frac{K n_a}{n_l} - A_g^o \left(\frac{K n_g}{n_l} + 1\right)\right]}{\left[\frac{K n_a}{n_l} - A_g \left(\frac{K n_g}{n_l} + 1\right)\right]} = k_2 t \qquad (15)$$

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 (15). The initial concentration of argon, $A_g^{\circ}$, 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 $\text{hours}^{-1}$. 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 IX 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 X.

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 XI. 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 $\text{hours}^{-1}$ compared to the average value of 0.027 $\text{hours}^{-1}$ found from the data in Table X. In view of the fact that the values in Table X were rather close to equilibrium the value of 0.05 $\text{hours}^{-1}$ 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:

$T = 88.42°K.$

$P = 707.90$ mm.

Mol % $O_2$ in gas = 73.31

Mol % A in gas = 26.69

Mol % $O_2$ in liquid = 80.80

Mol % A in liquid = 19.20

$Y/X = 1.390$

$Y/X$ from plot at 88.5°K. = 1.395

This value of 1.390 for the equilibrium constant at 88.42°K. corrected to 88.5°K. is 1.398.

The accuracy of the data was tested using the Duhem equation as shown in the next section.

__An Investigation of the Accuracy of Equilibrium Data for Some Binary Systems by Means of the Duhem Equation.__

The Duhem equation expressed in its most general form is

$$\sum N_i dF_i = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

for a two phase system this reduces to

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

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

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

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

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

$$\log \frac{a_1}{N_1} = - \int_0^{N_2} \frac{N_2}{N_1}\, d \log \frac{a_2}{N_2} \quad \ldots\ldots\ldots (6)$$

Assuming the vapor to be ideal, the data on the $A-O_2$ system and the $N_2-O_2$ system can be correlated by the use of this equation.

for a solute $a_2/N_2 = 1$ when $N_2 = 0$

Since we have assumed that the vapor is a perfect gas, then $a_2 \propto P_2$ and as we pass from a mol fraction $N_2$ to an infinitely dilute solution $N_2^*$

$$\frac{a_2}{P_2} = \frac{a_2^*}{P_2^*} \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

from Henry's Law $\frac{N_2}{P_2}$ approaches a constant value at infinite dilution denoted by $\frac{N_2^*}{P_2^*}$.

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

thus $a_2 = P_2 \frac{N_2^*}{P_2^*}$ and $\frac{a_2}{N_2} = P_2/N_2 \big/ P_2^*/N_2^*$ ............(8)

For the solvent, by definition

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

$$a_1 = \frac{f_1}{f_{1o}} = \frac{P_1}{P_{1o}} \quad \ldots\ldots\ldots\ldots\ldots (9)$$

Table XII gives the values of $a_1$ calculated from (9) (Col.2) and also the values of $a_1$ calculated from (6) (Col.3) for our data (sec.a) and for the data of Bourbo and Ishkin* (Phys. Zeitschr. d Sowjetunion 10, 271, 1936) on the argon-oxygen system (Secs. b and c). Oxygen is here called the solvent (mole fraction $N_1$) and argon the solute (mole fraction $N_2$).

Table XIII is a similar table for the data of Dodge and Dunbar (J.A.C.S. 49, 591, 1927) (sec.a) and Inglis (Phil Mag (VI) 11, 640, 1906) (sec.b) on the nitrogen-oxygen system calling nitrogen the solvent ($N_1$) and oxygen the solute ($N_2$).

Table XIV shows the effect of errors in the measured $a_1$ on the agreement between $a_1$ as measured and as calculated using the Duhem equation. Column 1 gives the value of $N_1$ column 2 gives percentage by which $P_1$ was arbitrarily changed from the data to get values of $a_1$ given in column 3. Column 4 gives the value of $a_1$ calculated from $a_2'$ by means of equation 6. The quantity $a_2'$ is the value calculated from $P_2'$ which is the total pressure minus $P_1 + \Delta P_1$ when $\Delta P_1$ is the change in $P_1$ corresponding to the percentage in column 2.

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* This is no more than a check on B & I's calculations for they used the Gibbs-Duhem equation to obtain their results.

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## Table I

### 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.

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Table I (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 |

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### Table I (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 | 753.99 | 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 |

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## Table II

## 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 |

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Table III

### 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 |

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Table IV

### TOTAL PRESSURE ABOVE ARGON-OXYGEN MIXTURES
### AT 88.57°K.

| Mole Per cent Argon in Liquid | Total Pressure 88.5°K. (int. mm.) |
|---|---|
| 0 | 638.3 |
| 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 |

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Table V

## EQUILIBRIUM DATA FOR THE SYSTEM ARGON-OXYGEN

| x<br>Mole Per cent of argon in liquid | y<br>Mole Per cent of argon in vapor | P<br>Total Pressure | K<br>(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 |

## Table VI

## 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 | |

Table VII

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 |

## Table VIII

### 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.

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### Table IX

### 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 |

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## Table X

### 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 |
| $N_s$ | 0.23220 | 0.1418 |
| $N_a$ | 0.04158 | 0.1171 |
| $A_g$ | 0.2325 | 0.7600 |
| $A_g^{\circ}$ | 0.2570 | 0.8290 |
| $t_2$ | 12 | 12 |
| $k_2$ | 0.0258 | 0.0290 |

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### Table XI

### 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 |

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## Table XII

| (a) **This Research** A-O isotherm at 88.5°K. | | | | (b) **Bourbo & Ishkin** A-O isotherm at 87°K. | | | | (c) **Bourbo & Ishkin** A-O isotherm at 90°K. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $O_2$ $N_1$ | $a_1=P_1/P_1°$ | $a_1$ (plot) | % diff. | $O_2$ $N_1$ | $a_1=P_1/P_1°$ | $a_1$ (plot) | % diff. | $O_2$ $N_1$ | $a_1=P_1/P_1°$ | $a_1$ (plot) | % diff. |
| 1.00 | 1.0000 | 1.0000 | 0 | 1.000 | 1.0000 | 1.0000 | 0 | 1.000 | 1.0000 | 1.0000 | 0 |
| .99 | .9906 | .9899 | .07 | .948 | .9532 | | | .960 | .9522 | .9607 | .90 |
| .98 | .9809 | .9799 | .10 | .850 | .8530 | .8517 | .15 | .868 | .8647 | .8706 | .47 |
| .90 | .9026 | .8993 | .36 | .749 | .7553 | .7545 | .10 | .770 | .7667 | .7759 | .10 |
| .85 | .8526 | .8488 | .45 | .635 | .6464 | .6493 | .45 | .657 | .6635 | .6689 | .81 |
| .80 | .8018 | .7992 | .32 | .545 | .5641 | .5645 | .07 | .558 | .5731 | .5737 | .10 |
| .75 | .7518 | .7508 | .13 | .445 | .4707 | .4688 | .41 | .442 | .4678 | .4664 | .30 |
| .70 | .7034 | .7026 | .10 | .330 | .3592 | .3568 | .67 | .350 | .3804 | .3805 | .03 |
| .60 | .6138 | .6121 | .31 | .264 | .2926 | .2913 | .44 | .241 | .2681 | .2689 | .30 |
| .50 | .5277 | .5245 | .61 | .142 | .1689 | .1686 | .18 | .166 | .1835 | .1897 | 3.31 |
| .40 | .4379 | .4337 | .98 | 0 | | | | 0 | | | |
| .30 | .3390 | .3332 | 1.71 | | | | | | | | |
| .20 | .2322 | .2278 | 1.91 | | | | | | | | |
| .10 | | | | | | | | | | | |
| 0 | | | | | | | | | | | |

## Table XIII

(a) **Dodge & Dunbar**
$N_2$-$O_2$ isotherm at 90.50°K.

| $(N_2)$ $N_1$ | $a_1$ plot | $a_1 = P_1/P_1°$ | % Dev. |
|---|---|---|---|
| 1.0000 | 1.0000 | 1.0000 | 0 |
| .8374 | .8416 | .8786 | + 4.2 |
| .6479 | .6647 | .6422 | - 3.5 |
| .5305 | .5565 | .5267 | - 5.6 |
| .5061 | .5344 | .5084 | - 5.1 |
| .4957 | .5249 | .4916 | - 6.7 |
| .4489 | .4826 | .4522 | - 6.8 |
| .3903 | .4289 | .3958 | - 8.3 |
| .2713 | .3204 | .2760 | -16.4 |
| .1940 | .2415 | .1983 | -21.0 |
| .1788 | .2249 | .1856 | -21.2 |
| .1759 | .2215 | .1824 | -21.4 |

(b) **Inglis**
$N_2$-$O_2$ isotherm at 74.70°K.

| $(N_2)$ $N_1$ | $a_1 = P_1/P_1°$ | $a_1$ plot | % Dev. |
|---|---|---|---|
| 1.0000 | 1.0000 | 1.0000 | 0 |
| .994 | - - - | - - - | --- |
| .939 | .9430 | .9405 | + .27 |
| .889 | .8959 | .8930 | + .32 |
| .840 | .8487 | .8561 | - .87 |
| .792 | .8044 | .7955 | +1.24 |
| .748 | .7626 | .7638 | - .16 |
| .686 | .7054 | .7099 | - .63 |
| .631 | .6551 | .6610 | - .89 |
| .573 | .6003 | .6088 | -1.4 |
| .564 | .5918 | .6006 | -1.5 |
| .522 | .5523 | .5624 | -1.8 |
| .484 | .5171 | .5272 | -1.9 |
| .445 | .4809 | .4910 | -2.0 |
| .418 | .4557 | .4654 | -2.1 |
| .375 | .4116 | .4238 | -2.9 |
| .334 | .3726 | .3828 | -2.7 |
| .305 | .3436 | .3531 | -2.7 |
| .256 | .2932 | .3026 | -3.2 |

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Table XIV

| $N_1$ | % offset on $P_1$ | $a_1 = P_1+\Delta P/P_1°$ (calc. from Col.2) | $a_1$ calc. from $a_2$ | % dev. | This Research<br>% error est. in $P_1$ | This Research<br>% error est. in K x/y |
|---|---|---|---|---|---|---|
| 1 | | | | | | |
| .99 | 0.1 | .9915 | .9900 | + .15 | .09 | 6.5* |
| .98 | 0.25 | .9832 | .9810 | + .21 | .10 | 3.6 |
| .90 | 1.05 | .9121 | .8994 | + 1.38 | .29 | 1.9 |
| .85 | 1.55 | .8657 | .8486 | + 1.98 | .45 | 1.6 |
| .80 | 2.15 | .8191 | .7981 | + 2.57 | .31 | 1.3 |
| .75 | 2.60 | .7721 | .7500 | + 2.86 | .12 | .2 |
| .70 | 3.15 | .7255 | .7014 | + 3.32 | .10 | .2 |
| .60 | 4.10 | .6390 | .6090 | + 4.70 | .29 | .3 |
| .50 | 5.0 | .5540 | .5195 | + 6.24 | .54 | .4 |
| .40 | 5.85 | .4636 | .4264 | + 8.02 | .82 | .4 |
| .30 | 6.80 | .3621 | .3237 | +10.6 | 1.31 | .4 |
| .20 | 7.80 | .2504 | .2164 | +13.6 | 1.28 | .2 |

* This value is probably not too reliable owing to the sensitivity of the lower values to the correct value of $P_1°$ and $P_2^*/N_2^*$.

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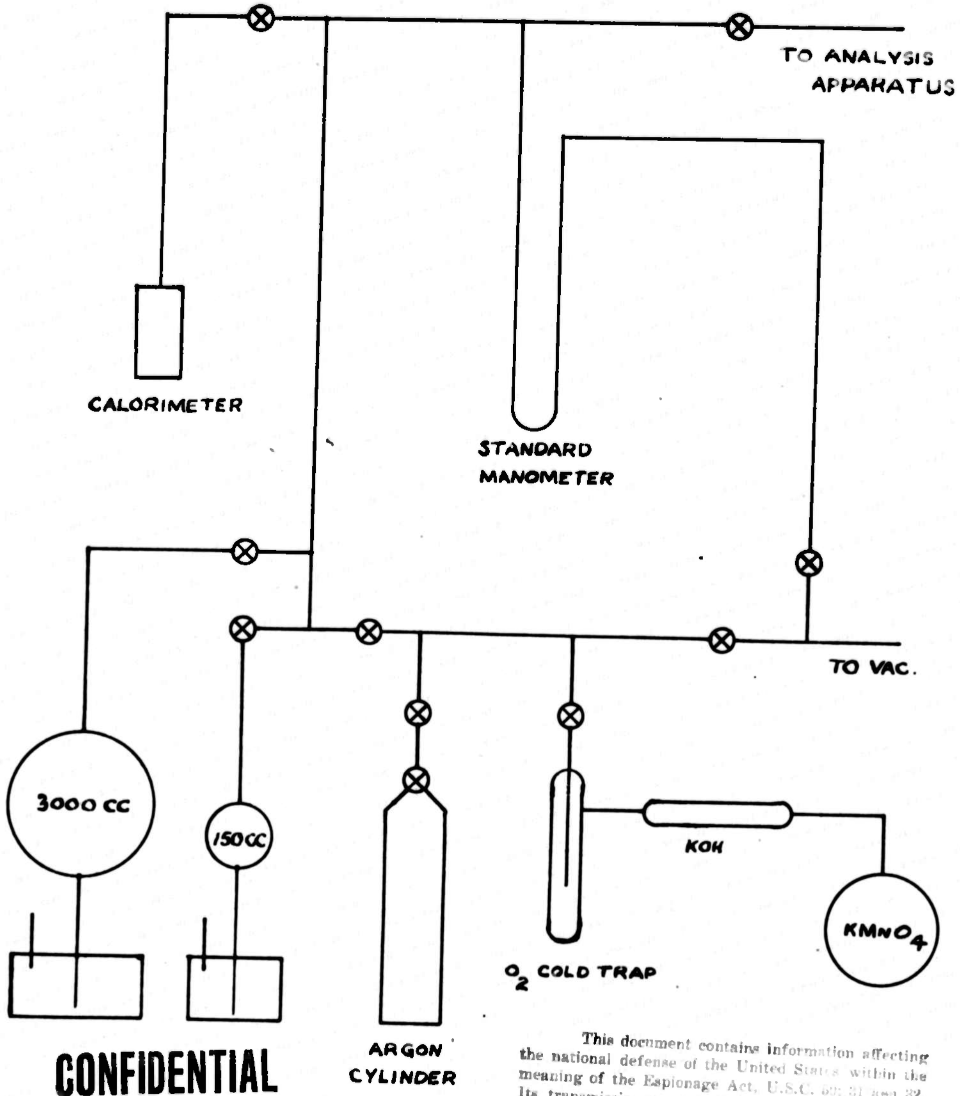

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LINES FOR EQUILIBRIUM MEASUREMENTS ON THE SYSTEM OXYGEN- ARGON

FIGURE -1

CRYOGENIC LABORATORY
THE PENNSYLVANIA STATE COLLEGE

GWM

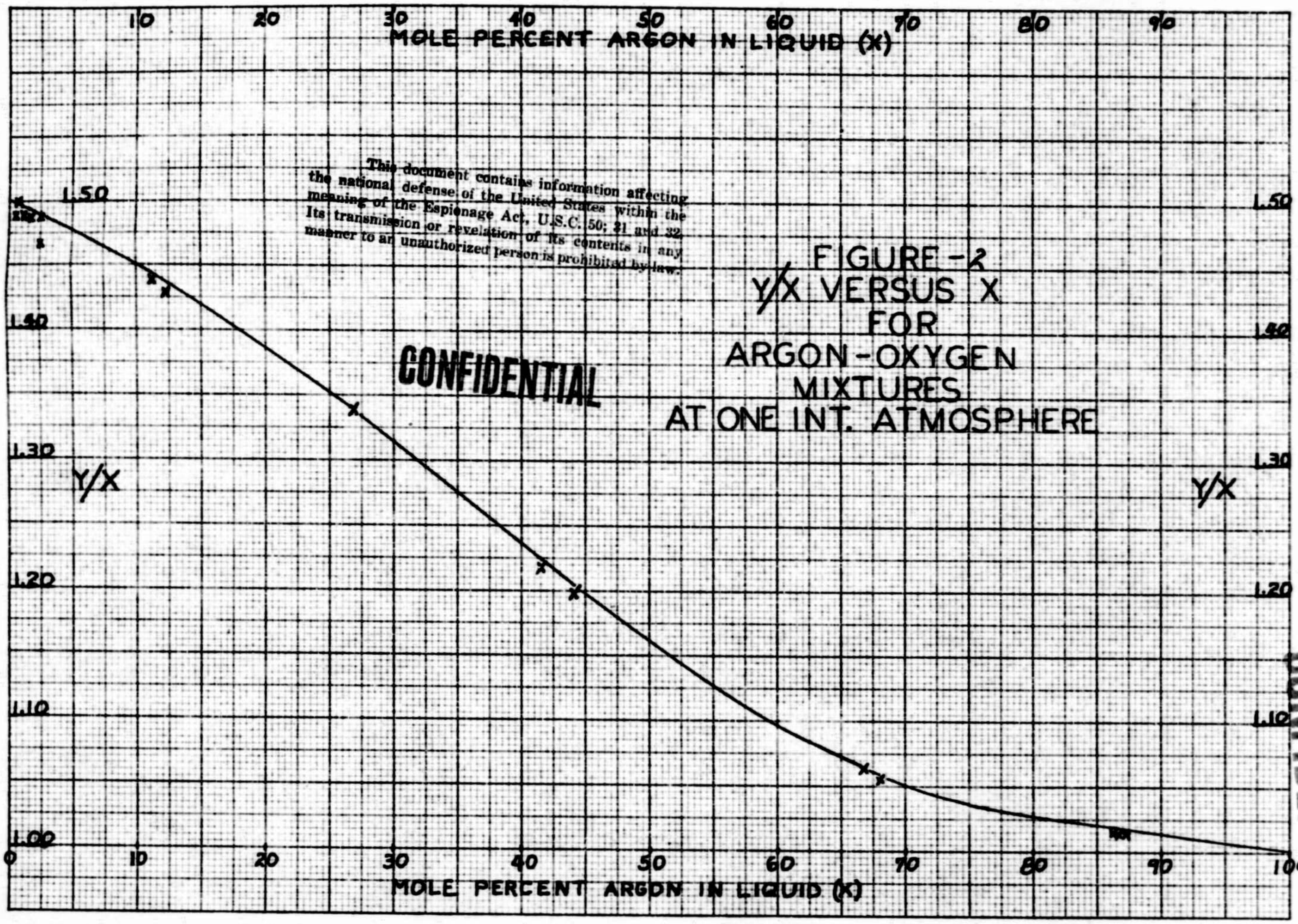

FIGURE-2
Y/X VERSUS X
FOR
ARGON-OXYGEN
MIXTURES
AT ONE INT. ATMOSPHERE

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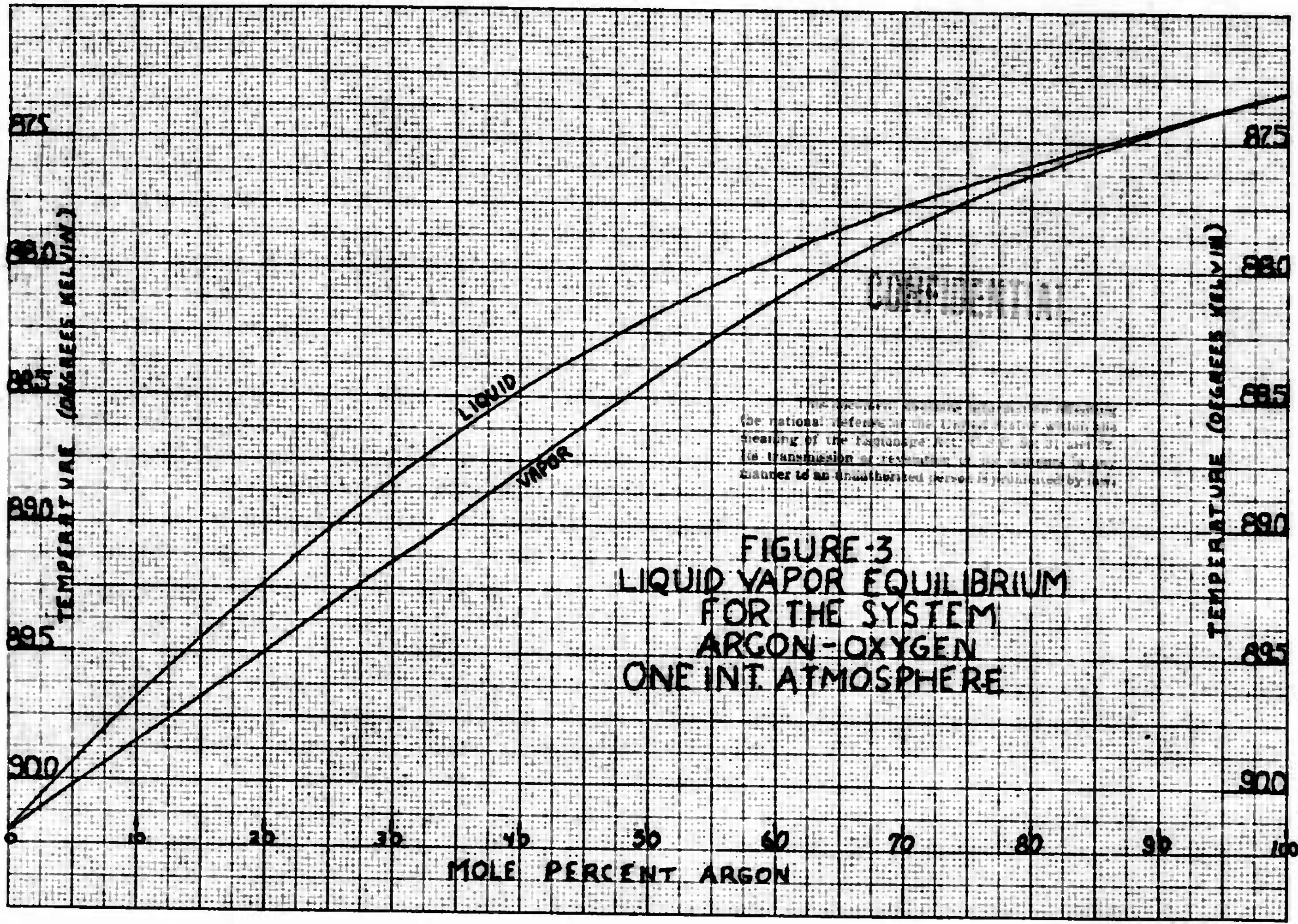

FIGURE-3
LIQUID VAPOR EQUILIBRIUM
FOR THE SYSTEM
ARGON-OXYGEN
ONE INT. ATMOSPHERE

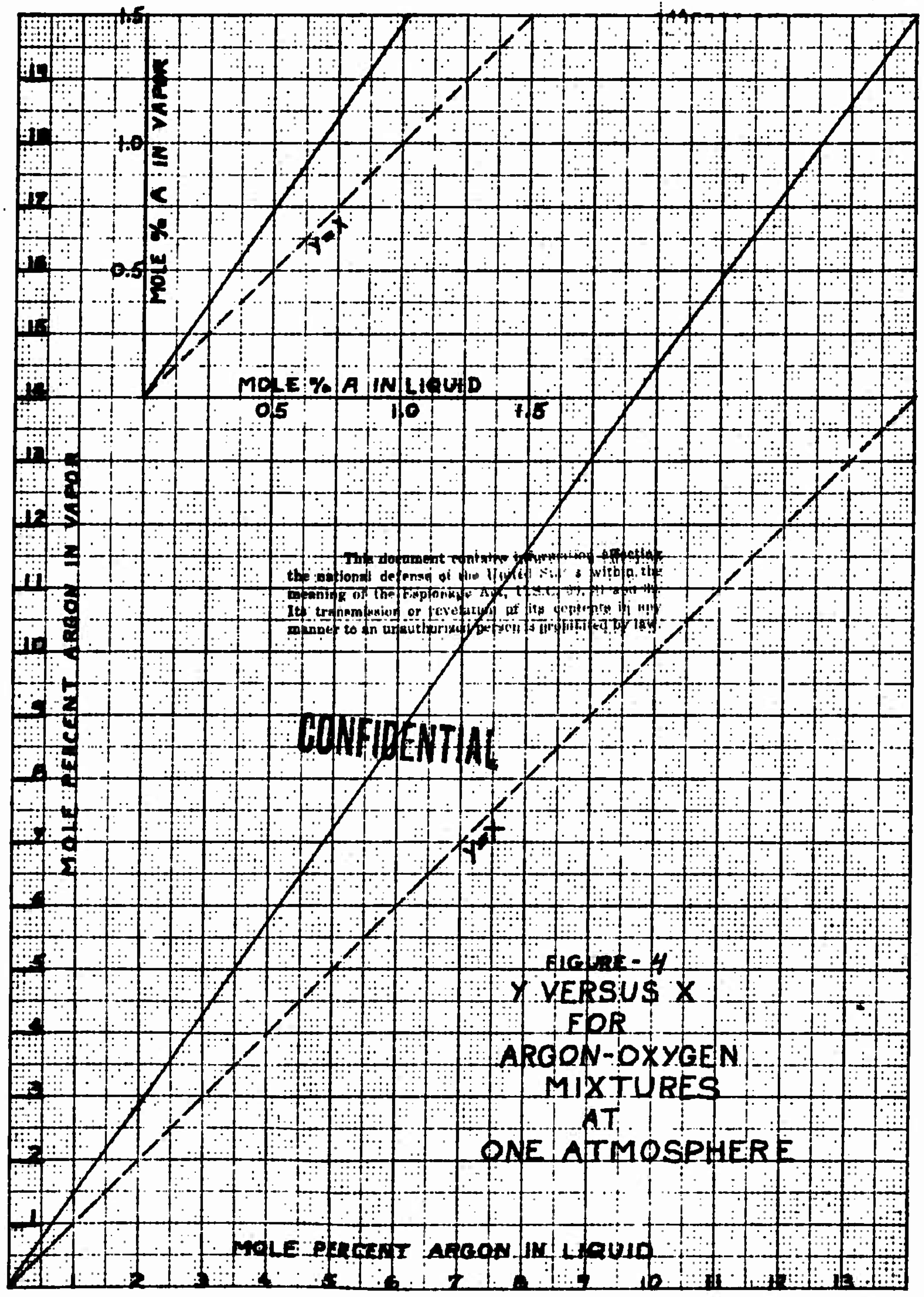

FIGURE - 4
Y VERSUS X
FOR
ARGON-OXYGEN
MIXTURES
AT
ONE ATMOSPHERE

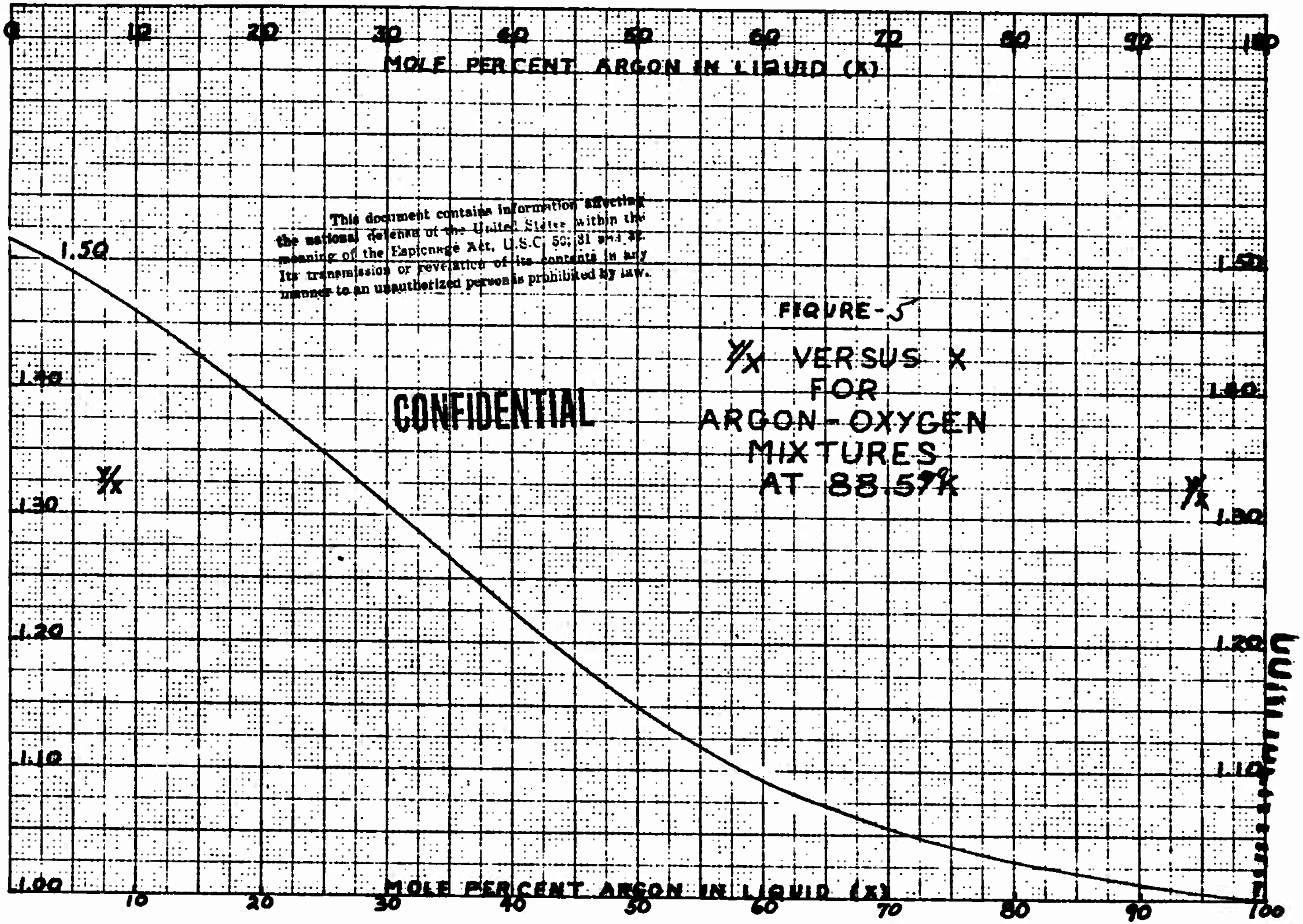

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FIGURE-5

y/x VERSUS x
FOR
ARGON-OXYGEN
MIXTURES
AT 88.57°K

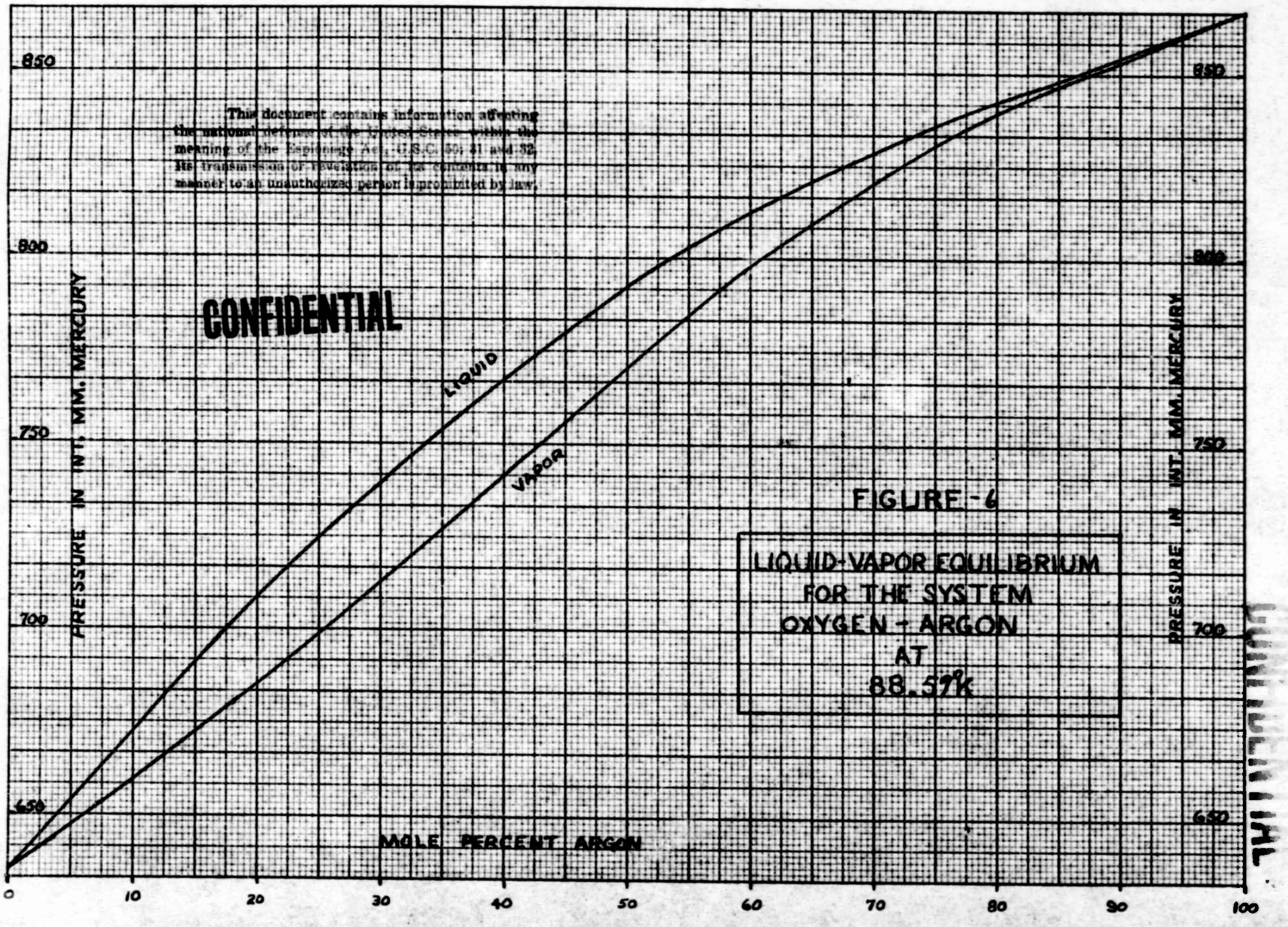

FIGURE - 6

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

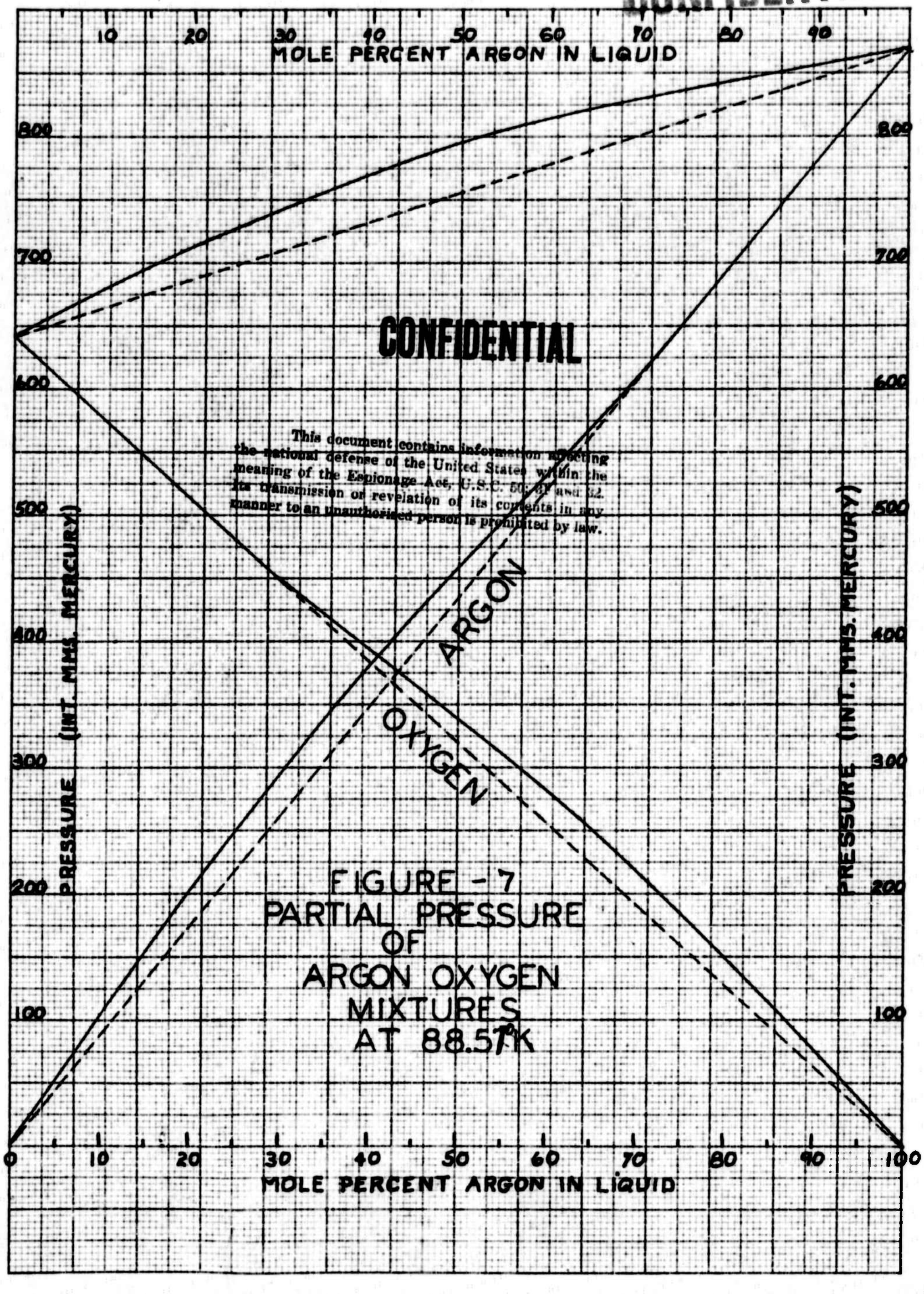

FIGURE - 7
PARTIAL PRESSURE
OF
ARGON OXYGEN
MIXTURES
AT 88.57°K

RFEL – C

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**ABSTRACT:**

The vapor pressure of certain liquid mixtures of argon and oxygen were measured, and the results were expressed by simple equations. From the data, normal boiling points of the liquid mixtures were computed as well as total pressures at 88.5°K. Compositions of the vapor and liquid in equilibrium were measured at one atmosphere total pressure over a wide range of concentration, and "K" values were compiled from the results. The composition of the vapor in equlibrium with the liquid was computed at 88.5°K over a wide range of composition. The partial pressures of argon and oxygen over a wide range of liquid composition at 88.5°K were found in accord with the Duhem equation. The Duhem equation was used to check the data on the oxygen-nitrogen system.

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TECHNICAL INDEX

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