

### Summary

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

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CRYOGENIC ENGINEERING LABORATORY OF HARVARD UNIVERSITY]

### VAPOR PRESSURE OF LIQUID OXYGEN AND NITROGEN

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### Introduction

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

### Previous Investigations

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

<sup>1</sup> Wroblewski, *Compt. rend.*, **98**, 982 (1884); *Sitzb. Akad. Wiss. Wien*, **91**, 705 (1885).

<sup>2</sup> Olszewski, *Compt. rend.*, **100**, 350 (1885).

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

<sup>4</sup> Baly, *ibid.*, [5] **49**, 517 (1900).

<sup>5</sup> Travers, Senter and Jaquerod, *Proc. Roy. Soc.*, **70**, 484 (1902).

<sup>6</sup> Bestelmeyer, *Ann. Physik*, **14**, 87 (1904).

<sup>7</sup> Onnes and Braak, *Comm. Leiden*, 107a, 1908.

<sup>8</sup> Germann, *Physik. Z.*, **14**, 857 (1913).

<sup>9</sup> Bulle, *ibid.*, **14**, 860 (1913).

<sup>10</sup> Von Siemens, *Ann. Physik*, **42**, 871 (1913).

<sup>11</sup> Henning, *ibid.*, **43**, 289 (1914).

<sup>12</sup> Onnes, Dorsman and Holst, *Comm. Leiden*, 145b, 1914.

<sup>13</sup> Cath, *ibid.*, 152d, 1918.

<sup>14</sup> Keyes, Townshend and Young, *J. Math. Phys. Mass. Inst. Tech.*, **1**, 243 (1922).

<sup>15</sup> Henning and Heuse, *Z. Physik*, **23**, 105 (1924).

Most of these investigations are in the region of pressures below one atmosphere and some involve only the determination of the normal boiling point. In spite of the large number of investigations of oxygen vapor pressure, there is only one reliable set of measurements at pressures greater than 1 atmosphere and that does not touch the region between 1 and 9 atmospheres. It is true that Germann and also Bulle made measurements in the region from 1–23.5 atmospheres, but their results are very erratic. Bulle's measurements were made with Germann's apparatus slightly modified, but the two do not agree very well, the difference in one case amounting to as much as  $0.9^{\circ}$ . Furthermore, the difference between the temperature given by our vapor-pressure equation and that observed by Germann at the same pressure varies from  $-0.04$  to  $+1.35^{\circ}$ , and the differences are not at all systematic.

The measurements for oxygen prior to 1913 are mainly of historical importance. The results of Von Siemens, of Cath, and of Henning and Heuse for the region between the triple point and the normal boiling point agree very well and hence this part of the vapor-pressure curve may be considered as sufficiently well established.

The vapor pressure of liquid nitrogen has been measured by Wroblewski,<sup>16</sup> Olszewski,<sup>17</sup> Baly,<sup>4</sup> Fischer and Alt,<sup>18</sup> Von Siemens,<sup>10</sup> Crommelin,<sup>19</sup> Onnes, Dorsman and Holst,<sup>12</sup> Cath<sup>13</sup> and Henning and Heuse.<sup>15</sup> The investigations prior to 1913 are of historical importance only, while the three since that time for the region below 1 atmosphere agree exceedingly well. Above 1 atmosphere there are only the measurements of Crommelin.<sup>20</sup>

In the calibration of the thermo-element used for temperature measurement and in checking our temperature scale, we have made use of vapor-pressure data for methane, so that it is pertinent at this point to review the previous investigations on this substance.

Vapor-pressure measurements of liquid methane<sup>21</sup> have been made by Wroblewski,<sup>16</sup> Olszewski,<sup>22</sup> Hunter,<sup>23</sup> Cardoso,<sup>24</sup> Henning and Stock,<sup>25</sup> and Keyes, Taylor and Smith.<sup>26</sup>

<sup>16</sup> Wroblewski, *Compt. rend.*, **102**, 1010 (1886).

<sup>17</sup> Olszewski, *ibid.*, **99**, 134 (1884).

<sup>18</sup> Fischer and Alt, *Ann. Physik*, [4] **9**, 1149 (1902).

<sup>19</sup> Crommelin, *Comm. Leiden*, 145d, 1914.

<sup>20</sup> Porter and Perry [THIS JOURNAL, **48**, 2059 (1926)] have recently measured vapor pressures of nitrogen above 1 atmosphere. Their paper was submitted a few months after the present one.

<sup>21</sup> Some unpublished measurements made at the Bureau of Standards were communicated to us by N. S. Osborne. These agree very well with the measurements of Keyes, Taylor and Smith, especially in the low-pressure range, and the agreement is exact at the normal boiling point.

<sup>22</sup> Ref. 2, p. 940.

<sup>23</sup> Hunter, *J. Phys. Chem.*, **10**, 330 (1906).

<sup>24</sup> Cardoso, *J. chim. phys.*, **13**, 332 (1915).

<sup>25</sup> Henning and Stock, *Z. Physik*, **4**, 226 (1921).

<sup>26</sup> Keyes, Taylor and Smith, *J. Math. Phys. Mass. Inst. Tech.*, **1**, 211 (1922).

### Experimental Method

Measurements were made by the static method, using the apparatus previously described in connection with an investigation of the binary system: oxygen-nitrogen.<sup>27</sup> In a few cases the static method was directly compared with a flow method in which the liquid was boiled and the vapor continuously recirculated through the liquid. Since no difference between the two methods was observed, the simpler static method was used in nearly all cases.

Some of the previous investigators have experienced trouble from superheating of the boiling liquids. We have had no trouble at all from this source, judging from the fact that the pressure and temperature of the boiling liquid could be held quite constant over a considerable period without the slightest evidence of any sudden jumps. The freedom from superheating may have been due to the fact that no very low pressures where this effect seems to be the greatest were measured, or to the design of the boiling vessel, which was such as to maintain a vapor-liquid interface below the main body of liquid.

The method of temperature measurement will require a more detailed description. A two-couple, copper-constantan thermo-element was used, the e.m.f. being measured on a slide-wire potentiometer which was calibrated during the course of this work by means of a series of standard resistances. The same standard cell that was used with the slide-wire potentiometer was also used in the potentiometer made up from the standard resistances. Its absolute e.m.f. is immaterial but its temperature coefficient is important. The latter was measured by "bucking" this standard cell against another and measuring the difference in their potentials by balancing this difference against a known  $IR$  drop. By maintaining the cell whose temperature coefficient was to be measured at various temperatures while the other cell was held at constant temperature, the measurement was made. It was found to be about  $-3$  microvolts per degree, which is quite negligible. The thermocouple installation was made in accordance with the directions given by White.<sup>28</sup>

The end of the copper protecting tube containing the couples was immersed for about 3 inches in the boiling liquid whose temperature was to be measured. The whole potentiometer set-up was shielded from stray currents by the method recommended by White, and his special circuit for parasitic elimination was also used. It was thus possible to read the e.m.f. of the element to about 0.5 microvolt and to reproduce any given reading within this amount. With the two-couple element, one microvolt corresponds to about  $0.03^{\circ}\text{C}$ . at  $90^{\circ}\text{K}$ .

To interpret the observed e.m.f.'s of the couple in terms of temperature,

<sup>27</sup> Dodge and Dunbar, *THIS JOURNAL*, 49, 591 (1927).

<sup>28</sup> White, *ibid.*, 36, 1856 (1914).

the couple was calibrated at three fixed points, the normal boiling points of nitrogen, oxygen and methane, respectively. The temperatures given in the literature for these fixed points may be found in Refs. 1-25.

The question of reduction from the gas scales to the thermodynamic scale is still in a very unsatisfactory state and we shall assume for the present no connection to the constant-volume helium or constant-volume hydrogen scales at the oxygen and nitrogen boiling points. The average of the results of the three latest investigations on oxygen is  $-182.97^{\circ}\text{C}.$ , and of the two latest on nitrogen is  $-195.80^{\circ}\text{C}.$

Assuming for the ice point on the absolute scale the value  $273.13^{\circ}\text{K}.$ , the following values were finally chosen for the three normal boiling points: nitrogen,  $-195.80^{\circ}\text{C}.$  ( $77.33^{\circ}\text{K}.$ ); oxygen,  $-182.97^{\circ}\text{C}.$  ( $90.16^{\circ}\text{K}.$ ); methane,  $-161.61^{\circ}\text{C}.$  ( $111.52^{\circ}\text{K}.$ ).

The preparation and storage of the pure oxygen and nitrogen have been described elsewhere.<sup>26</sup> Methane for use in calibration of the thermoelement was prepared from natural gas containing about 96% of methane by repeated fractionation. The gas was first scrubbed with concd. sulfuric acid, solid potassium hydroxide and phosphorus pentoxide, then liquefied using liquid oxygen as refrigerant. The liquid was evacuated to remove nitrogen and any other impurities more volatile than methane, about 10% of the liquid being distilled off in this manner. The remaining liquid was then slowly distilled to another bulb cooled with liquid oxygen, until a residue of about 15% remained which was discarded. This process was repeated four times, the final distillate being stored in a steel cylinder. One series of measurements was made with methane so prepared and this batch of methane was then further purified by three distillations and used in a second series of measurements, again purified and used in a third series. A fourth series was made with another batch of methane made from the same lot of natural gas by the above process, distilling the liquid six times. A fifth series of measurements was made on still another batch of methane from the same lot of natural gas, purified by six distillations. That the methane in all cases was substantially pure is shown by the fact that the average  $\Delta T$  ( $T$  obs.  $- T$  calcd. from an equation used to smooth the observations) was  $0.045^{\circ}\text{C}.$  for all the measurements. A further check on the purity of the methane was made in some cases by pumping off a considerable percentage of the liquid between two measurements and in those cases the differences in pressure were slight and well within the experimental error.

### Results

The corrected observations consisted of a series of e.m.f. readings in microvolts and a corresponding series of vapor pressures. To determine the e.m.f. of the couple at the chosen fixed points, the vapor pressures in atmospheres for each gas in the neighborhood of the normal boiling point

were plotted against the corresponding e.m.f.'s in microvolts, and from this curve the e.m.f. at 1 atmosphere was obtained. Fig. 1 shows the curve obtained for oxygen, which gives an idea of the consistency of the observations.

For interpolation between the fixed points and extrapolation beyond the methane point we have used an equation of the type proposed by Adams.<sup>29</sup>

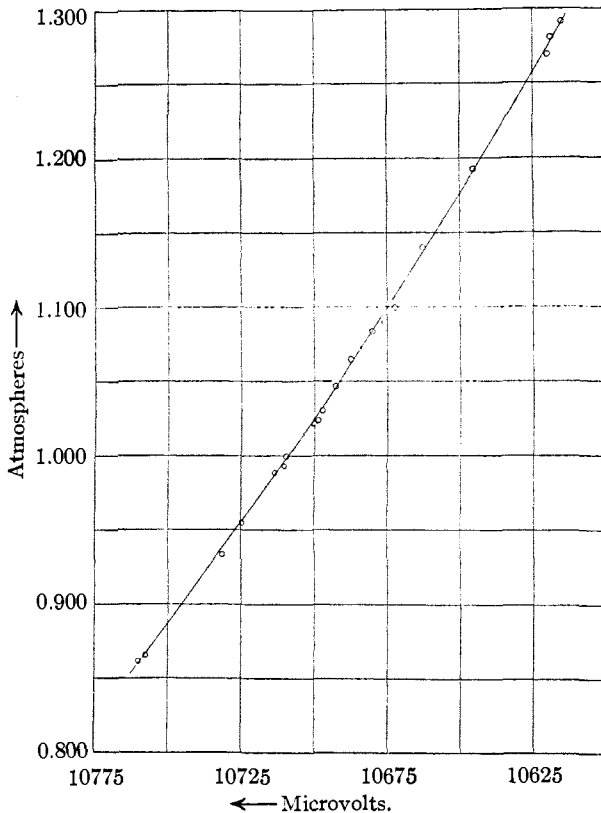


Fig. 1.—Plot of pressure against e.m.f. of the thermocouple for oxygen in the neighborhood of 1 atm.

Substitution of the values of e.m.f. and  $t$  at the three fixed points gave the equation

$$E = -131.8046t + 18331.8 (1 - e^{-0.00304t}) \quad (1)$$

where  $E$  is in microvolts and  $t$  in degrees centigrade. In order to find out to what extent the interpolation and extrapolation would depend on the particular equation chosen, we also fitted an equation of the type used by Keyes<sup>14</sup> to the data at the three points and obtained the equation

$$E = 0.01282t^{2.369} - 74.564t \quad (2)$$

<sup>29</sup> Adams, *Bull. Am. Inst. Min. Met. Eng.*, 153, 2111 (1919).

Table I gives a comparison of values calculated from the two equations. The agreement is remarkably good over the range covered in this investigation ( $t = -196$  to  $-139$ ) and leaves no doubt that either equation is very satisfactory.

TABLE I  
COMPARISON OF THE TWO THERMOCOUPLE EQUATIONS

$t$	$E$ (Keyes)	$E$ (Adams)	$\Delta E$	$\Delta t$
-200	11290.0	11290.0	0.0	0
-170	10210.7	10210.9	.2	<0.01
-151.13	9403.4	9403.8	.4	< .01
-140	8882.7	8884.2	1.5	.03
-100	6755.1	6766.9	11.8	.20

Our e.m.f. values were changed to temperatures by means of the table of e.m.f. against temperature published by Adams<sup>29</sup> supplemented by a deviation plot giving the difference between the e.m.f. of our couple and Adams', calculated with the aid of Equation 1. Adams' table gives the temperature for every 200 microvolts for a two-couple element and in order to interpolate more accurately we have extended his table to give the temperature for every 10 microvolts.

A summary of the final data for oxygen and nitrogen is given in Table II. Each point represents an average of two or more observations.

TABLE II  
SUMMARY OF FINAL VAPOR-PRESSURE DATA  
1. Nitrogen

$T$ , °K.	$P$ , atm.	$\Delta T_{II}$ (calcd.-obs.)	$\Delta T_{II}$	$T$ , °K.	$P$ , atm.	$\Delta T_{II}$ (calcd.-obs.)	$\Delta T_{II}$
76.34	0.8885	+0.07	+0.02	101.63	8.591	-0.11	+0.02
76.94	.9529	+ .06	- .03	102.12	8.865	- .14	.00
77.35	1.0001	+ .06	- .02	102.42	9.080	- .08	+ .06
77.52	1.0234	+ .09	+ .01	103.48	9.700	- .15	- .01
78.23	1.1090	+ .07	.00	105.85	11.297	- .14	.00
79.44	1.2717	+ .08	+ .02	108.26	13.106	- .13	.00
83.67	1.9575	- .06	- .08	110.74	15.156	- .13	- .03
87.33	2.775	- .09	- .07	111.06	15.464	- .10	.00
90.49	3.682	- .07	- .01	113.92	18.123	- .06	- .02
90.54	3.711	- .02	+ .03	114.48	18.725	- .10	- .05
90.66	3.759	.00	+ .06	115.04	19.298	- .05	- .02
90.68	3.743	- .06	- .01	117.84	22.258	- .09	- .14
90.73	3.746	- .10	- .05	118.29	22.870	- .01	- .06
91.93	4.168	- .04	+ .03	121.48	26.985	+ .20	+ .02
94.53	5.133	- .06	+ .03	121.83	27.456	+ .22	+ .02
2. Oxygen							
77.44	0.2076	-0.20	-0.16	93.53	1.3962	+0.02	-0.01
78.80	.2552	- .07	- .05	94.40	1.5151	.00	- .03
80.96	.3426	- .02	+ .01	98.41	2.183	+ .01	- .03
83.01	.4428	- .02	- .01	98.74	2.260	+ .09	+ .04
84.31	.5190	- .01	- .01	99.48	2.3847	- .03	- .07

TABLE II (Concluded)

$T, ^\circ\text{K.}$	$P, \text{atm.}$	$\Delta T_{\text{I}}$ (calcd.-obs.)	$\Delta T_{\text{II}}$	$T, ^\circ\text{K.}$	$P, \text{atm.}$	$\Delta T_{\text{II}}$ (calcd.-obs.)	$\Delta T_{\text{II}}$
86.19	.6444	- .03	- .03	101.11	2.745	+ .02	- .03
87.75	.7707	+ .02	+ .01	102.50	3.079	+ .04	- .01
88.77	.8616	+ .03	+ .01	104.17	3.516	+ .05	.00
88.84	.8658	.00	- .01	105.49	3.876	.00	- .05
89.56	.9336	- .01	- .02	106.43	4.160	.00	- .05
89.74	.9553	+ .03	+ .01	107.85	4.621	- .01	- .03
90.05	.9889	+ .05	+ .04	109.84	5.317	- .01	- .05
90.13	.9931	+ .01	.00	113.32	6.7195	- .04	- .07
90.14	.9999	+ .07	+ .05	115.25	7.631	- .01	- .02
90.41	1.0219	+ .01	- .01	117.25	8.631	- .03	- .04
90.44	1.0238	.00	- .02	120.24	10.273	- .12	- .10
90.49	1.0303	+ .01	- .01	121.70	11.209	- .07	- .04
90.60	1.0468	+ .05	+ .03	122.41	11.683	- .05	- .02
90.75	1.0646	+ .07	+ .05	125.57	13.941	- .03	+ .03
90.96	1.0834	+ .03	+ .01	126.29	14.433	- .06	+ .01
91.07	1.0892	- .03	- .05	126.58	14.651	- .07	+ .01
91.16	1.0995	- .03	- .05	129.97	17.374	- .14	- .03
91.41	1.1400	+ .08	+ .06	129.90	17.418	- .02	+ .04
91.90	1.1929	+ .04	+ .02	130.40	17.814	- .07	+ .05
92.59	1.269	- .02	- .05	131.97	19.285	- .06	+ .07
92.62	1.2804	+ .04	+ .01	134.22	21.470	- .02	+ .16
92.72	1.2910	+ .02	.00				

For purposes of interpolation, equations have been fitted to our observations. It was found that  $\log P$  was very nearly a linear function of  $1/T$  in all cases. In fact, it is hardly necessary to use anything but this very simple equation to represent completely the vapor pressures of oxygen, nitrogen and methane all the way from the triple point to the critical point. When  $\Delta \log P$  ( $\log P$  calculated from the linear relation minus  $\log P$  observed) was plotted against  $1/T$ , a slight systematic deviation from zero was obtained, showing that further terms should be added to the equation. By drawing the best representative line through the deviations and choosing 3 or 4 points on this curve a deviation equation was obtained which, combined with the original  $\log P$  against  $1/T$  equation, gave the final vapor-pressure equation. Representing the linear equation by

$$\log P = (A'/T) + B' \quad (3)$$

and the final equation by

$$\log P = (A/T) + B + CT + DT^2 \quad (4)$$

the various constants for  $P$  in atmospheres and  $T$  in  $^\circ\text{K.}$  are given in Table III. The constants for the less exact linear equation are given because it

TABLE III  
CONSTANTS OF EQUATIONS 3 AND 4

	$A'$	$B'$	$A$	$B$	$C$	$D$
Oxygen	-366.523	4.06295	-372.808	4.18939	-0.0006195	0
Nitrogen	-304.494	3.93352	-316.824	4.47582	- .0071701	$2.940 \times 10^{-8}$

is a very convenient one to use and is almost as accurate as the more complex equation.

The agreement between Equations 3 and 4 and the observations is shown in Table II under the headings  $\Delta T_I$  and  $\Delta T_{II}$ , respectively ( $\Delta T$  is in each case  $T$  calcd. -  $T$  obs.).

### Discussion of Results

Our results for oxygen agree well with those of Cath and of Henning and Heuse for the region around 1 atmosphere, as would be expected from the fact that we chose the oxygen normal boiling point as determined by these observers as one of our fixed points. It is mainly the values above 1 atmosphere that are interesting, since few data exist in this range. In Table IV is given a comparison between our data and some unpublished measurements by Dunbar and Davis.

TABLE IV  
COMPARISON WITH DATA OF DUNBAR AND DAVIS

$T$ , °K.	$P$ (Dunbar)	$P$ (Dodge)	$\Delta T$
77.63	0.2172	0.2182	-0.03
81.12	.3485	.3494	-.02
88.04	.7944	.7949	.00
94.04	1.469	1.468	+.01
100.04	2.518	2.517	.00
105.04	3.760	3.759	.00
110.04	5.409	5.411	-.01
115.04	7.531	7.541	-.02
120.04	10.193	10.216	-.04
125.04	13.457	13.503	-.06
130.04	17.378	17.457	-.09

The agreement is excellent, especially in view of the fact that Dunbar and Davis used only two fixed points, the oxygen and nitrogen normal boiling points, in calibrating their thermocouple. The only other measurements noteworthy in this range are those of Onnes, Dorsman and Holst, and in Table V is given a comparison with our own.

TABLE V  
COMPARISON WITH DATA OF ONNES, DORSMAN AND HOLST

$T$ , °K.	$P$ (Onnes, Dorsman and Holst)	$P$ (calcd. from Dodge equation)	$\Delta T$
118.26	9.096	9.198	-0.18
123.88	12.506	12.683	-.25
134.18	21.328	21.274	+.05
142.49	30.914	(30.531) <sup>a</sup>	+.29

<sup>a</sup> Calculation of this value involved an extrapolation of the data.

The comparison of our nitrogen equation with the equations of Cath, of Henning and Heuse, and Crommelin is given in Table VI. ( $\Delta T_I$ )



TABLE VI  
COMPARISON OF OUR NITROGEN EQUATION WITH THE EQUATIONS OF OTHER  
INVESTIGATORS

$T$ , °K.	$P$ , atm.	Observer	$P$ calcd.	$\Delta T_I$	$\Delta T_{II}$
77.29	0.9904	Cath	0.9936	-0.03	....
79.22	1.238	Cath	1.239	- .01	....
82.47	1.754	Cath	1.749	+ .03	....
84.25	2.095	Cath	2.089	+ .03	....
82.47	1.773	Henning and Heuse	1.749	+ .13	....
80.00	1.273	Crommelin	1.349	- .53	+0.05
85.00	2.198	Crommelin	2.246	- .22	....
90.00	3.507	Crommelin	3.535	- .09	+ .03
95.00	5.278	Crommelin	5.309	- .08	....
100.00	7.605	Crommelin	7.666	- .11	+ .01
105.00	10.593	Crommelin	10.708	- .17	....
110.00	14.358	Crommelin	14.542	- .22	- .06
115.00	19.036	Crommelin	19.279	- .24	....
120.00	24.772	Crommelin	25.036	- .22	- .26
125.00	31.730	Crommelin	31.940	- .15	....
126.00 <sup>a</sup>	33.284	Crommelin	33.471	- .13	- .49

<sup>a</sup> Critical temperature.

The agreement with Crommelin is not very good, but Crommelin's own observations do not agree well with his equation. Furthermore, Crommelin notes that his point at  $T = 81.25^\circ\text{K}$ . is "considerably less accurate than the other ones," and yet he has used that point in the determination of the constants in his equation. Crommelin states that his equation satisfies the values of the critical constants as given by Onnes, Dorsman and Holst, but such is not the case. Our own equation gives a critical pressure which agrees almost exactly with that of Onnes, Dorsman and Holst when their value of the critical temperature is used. Cath fitted another equation to Crommelin's data in an attempt to reconcile them with his own measurements. The agreement between this equation<sup>30</sup> and our own ( $\Delta T_{II}$  in Table VI) is excellent up to 15 atmospheres, but above that a considerable deviation occurs. As in the case of oxygen, our nitrogen results agree excellently with some unpublished results obtained in this Laboratory by Dunbar and Davis.

Fig. 2 shows how well the simple linear  $\log P$  against  $1/T$  equation fits the observations for both oxygen and nitrogen over a very wide range. The lines are the graphs of Equation 3, using the appropriate constants from Table III. The points are plotted from our observations, and from those of Cath and of Onnes, Dorsman and Holst, where the line passes beyond the range of our observations. The complete vapor-pressure curve for liquid nitrogen is shown and for oxygen the curve runs from a pressure of 0.05 to 49.71 atmospheres, the critical pressure. The log

<sup>30</sup>  $T \log P = 190.86 + 3.9649(T - T_k) + 0.00100(T - T_k)^2$ .

$P$  against  $1/T$  equation is derived from the Clausius-Clapeyron equation with the aid of the three following assumptions: (1) that the vapor behaves as an ideal gas; (2) that the volume of the liquid is negligible in comparison with that of the vapor; (3) that the heat of vaporization is constant. No one of these assumptions is even very approximately true over the

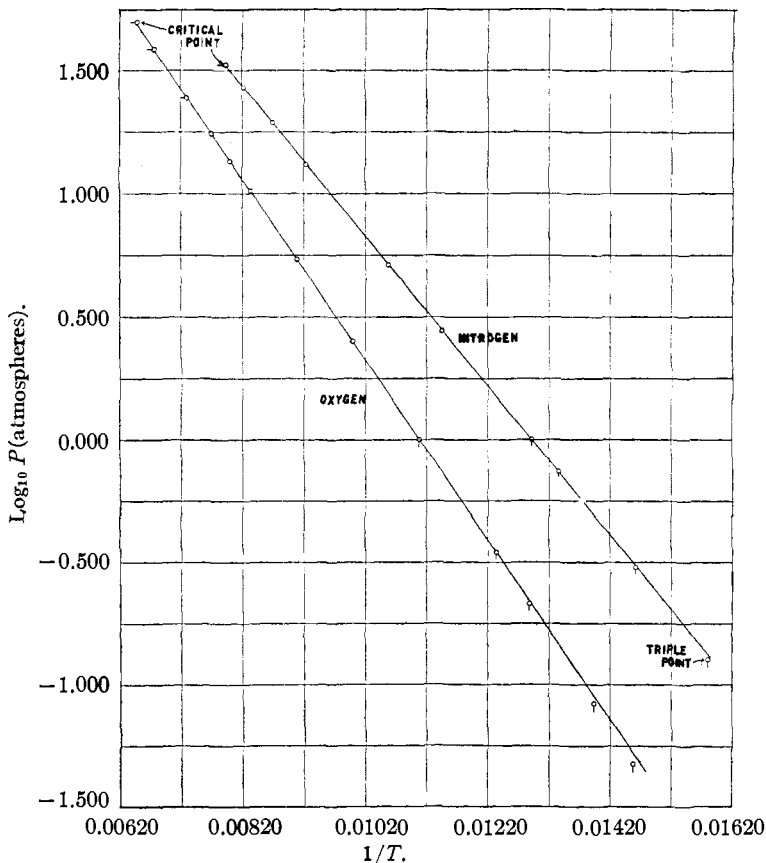


Fig. 2.—Logarithm of the pressure against the reciprocal of the absolute temperature for oxygen and nitrogen. ○, Dodge and Davis; ◻, Cath; -○, Onnes, Dorsman and Holst.

ranges here involved; in fact the deviations from (2) and (3) are relatively enormous and yet the relation holds with remarkable exactness, which would seem to indicate that a peculiar compensation of errors was in some way taking place.

### Summary

Using an apparatus developed for the study of liquid-vapor mixtures of oxygen and nitrogen, the vapor pressure of pure liquid nitrogen has been

measured from the normal boiling point to the critical point and of pure liquid oxygen from 0.2 to 21 atmospheres. The following equations have been fitted to the data: oxygen,  $\log_{10} P$  (atm.) =  $-372.808/T + 4.18939 - 0.0006195T$ ; nitrogen,  $\log_{10} P$  (atm.) =  $-316.824/T + 4.47582 - 0.0071701T + 2.940 \times 10^{-3}T^2$ . The following simpler equations, while not quite as good as the above equations, also reproduce the data very well: oxygen,  $\log_{10} P$  (atm.) =  $-366.523/T + 4.06295$ ; nitrogen,  $\log_{10} P$  (atm.) =  $-304.494/T + 3.93352$ . It has also been shown that the linear  $\log P$  against  $1/T$  equations hold exceedingly well for nitrogen over the whole liquid line from the triple point to the critical point, and for oxygen over an even wider range of pressures, namely, from 0.05 to 49.7 atmospheres (critical pressure).

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[CONTRIBUTION FROM GENERAL LABORATORIES, UNITED STATES RUBBER COMPANY]

## VOLUME CHANGES ATTENDING THE FORMATION OF RUBBER SOLS. I<sup>1</sup>

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The purpose of the present investigation was to discover: (1) whether or not there is a volume change when rubber goes into solution, and (2) whether the condition of the rubber has any effect on this.

### Introduction

It is well known that the formation of a solution is in general attended by a change in the total volume of the constituents. This volume change usually takes the form of a contraction, but may in some cases be an expansion, for example, sodium palmitate-water;<sup>1a</sup> *p*-nitrotoluene-carbon disulfide.<sup>2</sup> Volume changes may be referred to three effects:<sup>3</sup> to the cohesive affinities involved, to the effect of polymerization or association of one or both of the substances concerned and to their compressibilities. The first effect is comparable to the volume change which solids and liquids undergo on chemical combination, and includes the tendency to formation of complex molecules between solute and solvent, that is, solvation. There is considerable evidence indicating that dilution of a substance brings about a gradual depolymerization in a polymerized substance, and that solution tends to diminish the degree of polymerization.

<sup>1</sup> This paper was read at the meeting of the Rubber Division of the American Chemical Society held at Akron, Ohio, February 22-23, 1926.

<sup>1a</sup> McBain, "Third Report on Colloid Chemistry and Its General and Industrial Applications," 1920, p. 14.

<sup>2</sup> Hyde, THIS JOURNAL, 34, 1507 (1912).

<sup>3</sup> Richards and Chadwell, *ibid.*, 47, 2283 (1925).