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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 2969

THE CONDENSATION LINE OF AIR AND THE HEATS OF VAPORIZATION OF OXYGEN AND NITROGEN

By George T. Furukawa and Robert E. McCoskey

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SUMMARY

The condensation pressure of air was determined over the range of temperature from 60° to 85° K. The experimental results were slightly higher than the calculated values based on the ideal solution law.

Heat of vaporization of oxygen was determined at four temperatures ranging from about 68° to 91° K and of nitrogen similarly at four temperatures ranging from 62° to 78° K.

INTRODUCTION

In view of the low temperatures and the consequent condensation processes encountered in hypersonic wind-tunnel research, a program was initiated at the National Bureau of Standards for the determination of the basic properties of liquid air and its components to aid in the development of the theory of condensation in wind tunnels. The properties to be determined in the investigation were the condensation line of air, the heats of vaporization of oxygen and nitrogen, and the surface tension of air and its components. This report constitutes the results of the measurements involving the first two properties. The surface-tension measurements are yet to be made. The condensation line was determined from 60° to 85° K. The heat of vaporization of oxygen was determined at four temperatures ranging from 68° to 91° K and of nitrogen similarly at four temperatures ranging from about 62° to 78° K.

This work was conducted under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics. The authors are grateful to Messrs. W. Bruenner and M. L. Reilly of the NBS for their assistance with some of the experimental work.

APPARATUS AND METHOD

As the data for the condensation line of air were urgently needed a method was used in which the existing apparatus was readily applicable although the data obtainable were not considered to be extremely accurate. The condensation pressure of air was determined by successively introducing into a thermostated container measured quantities of air freed of carbon dioxide and water. The observed pressures were plotted as a function of the amounts of air added, and the intersection of the straight line representing the gas phase and of that representing the vapor-liquid phases was taken to be the condensation pressure at the given temperature. In these measurements an adiabatic calorimeter served as a thermostated container. The design and the operation of the calorimeter have been previously described in the paper on 1,3-butadiene by Scott and others (ref. 1). The quantity of air admitted into the calorimeter was determined volumetrically at a known temperature (about 26° C). The temperature of the calorimeter and its contents rose after each addition of air, because the air introduced into the calorimeter was at a higher temperature. The temperature in the calorimeter was restored by first cooling below the desired temperature and then heating. The pressure was read after temperature equilibrium using a mercury manometer and a mirror-backed calibrated glass scale. The pressure readings were converted to standard millimeters of mercury (gravity, 980.665 cm sec^{-2}; temperature, 0° C) on the basis that the local gravity is 980.076 cm sec^{-2}.

The heat-of-vaporization experiments were carried out using a different calorimeter, similar in design to the calorimeter used in the condensation-line experiments except for a valve placed on the filling tube within the space surrounded by the adiabatic shield. A similar calorimeter has previously been described by Aston and others (ref. 2). Briefly, in the vaporization experiments a known electrical power was supplied continuously to evaporate the material. The vapor was removed isothermally from the calorimeter by controlling the valve and was condensed in a high-pressure cylinder (230 ml) using liquid hydrogen as the refrigerant. The weighings were made using an H. Troemner balance of 2-kg capacity. The electrical power, time, and temperature measurements as well as other calorimetric procedures were similar to those previously described in reference 1.

In the vaporization experiments part of the material vaporized remains in the calorimeter to occupy the space left by the vaporized liquid or solid. The total electrical energy Q and the mass m of the material collected are related to the heat of vaporization per unit mass l by

$$\frac{Q}{m} = l\left(\frac{V}{V - v}\right) = l + Tv\,\frac{dp}{dT} \qquad (1)$$

where V and v are the specific volumes of the vapor and condensed phases, respectively, p is the vapor pressure, and T is the temperature of vaporization. In the series of results presented in this report, the maximum value of the conversion term $Tv\,\frac{dp}{dT}$ amounted to 0.6 percent (nitrogen).

SAMPLES

The air used in these measurements was atmospheric air freed of carbon dioxide and water by passing through a tube containing Ascarite and calcium chloride. As air is considered practically uniform in composition, no analysis was made. In this report air is considered to be a ternary system containing 0.7811, 0.2096, and 0.0093 mole fraction of nitrogen, oxygen, and argon, respectively. These figures were computed from the composition of various gases in dry air at the normal sea level as given by Humphreys (ref. 3) on the basis that the gases other than these three were absent.

The oxygen sample was prepared by thermal decomposition of potassium permanganate as given by the reaction:

$$2KMnO_4 (200^\circ\text{-}250^\circ\ C) \longrightarrow MnO_2 + K_2MnO_4 + O_2$$

The usual precautions of eliminating adsorbed gases on the surfaces of the generating and collecting systems were taken. The first 10 percent of the oxygen generated was discarded. This procedure served to purge the system and to rid it of any volatile impurities present in the potassium permanganate. Although the material used was of reagent grade, a considerable amount of water was generated. The latter was removed by means of a dry-ice - acetone cold trap. The purity of the product was determined from the equilibrium melting temperatures (ref. 4). In this method known amounts of the material are melted and the corresponding equilibrium temperatures are measured. The temperatures are plotted as the function of the reciprocal of the fraction melted $1/F$, where F is the fraction melted. The product of the slope of the curve and the cryoscopic constant $-L/RT_t^2$ is the mole-fraction impurity, where L is the heat of fusion, R the gas constant, and T_t the triple-point temperature. The method, however, involves certain assumptions. The solution is considered to obey Raoult's law throughout the range of concentration, and the impurities are considered to remain in solution without forming a solid solution with the major component. The results of the purity determination with the oxygen are given in table 1 and figure 1. The purity as computed from the slope of the curve was 99.997 mole percent. The temperature intercept, $1/F = 0$, is taken to be the triple-point temperature, and this value was 54.370° K.[1] The cryoscopic constant was taken to be -0.0181 deg^{-1} in which the value of the heat of fusion used was 444.7 abs j mole^{-1} (ref. 5).

The nitrogen was a high-purity dry nitrogen obtained from The Linde Air Products Co. This material was used without additional purification. Its purity was determined from the equilibrium melting temperatures and the results of the measurements are given in table 2 and figure 2. The purity found was 100.000 mole percent and the triple-point temperature was 63.180° K. The cryoscopic constant was taken to be -0.0217 deg^{-1} and the heat of fusion used was 720.9 abs j mole^{-1} (ref. 6). The purity specification given by The Linde Air Products Co. was maximum argon and other inert gas impurities, 100 parts per million; and maximum other impurities, 100 parts per million.

RESULTS

Condensation Pressures

The results of the condensation-pressure determination are given in table 3 and in figures 3(a) to 3(h). The figures give the pressure at the intersection and the corresponding temperature. Figure 4 shows a semilogarithmic plot of the condensation pressure as a function of the temperature. The vapor-pressure - composition results of Inglis (ref. 7) and Dodge and Dunbar (ref. 8) with the oxygen-nitrogen solutions were plotted on a large scale and the dew-point pressures at 21 percent oxygen and 79 percent nitrogen were obtained. These values together with the values based on Raoult's law are plotted for comparison in figure 4, which shows the experimental results to be slightly higher. The condensation curve in the range of temperature from 60° to 65° K is drawn broken as solid phase is also expected to be formed in this range.

As shown in figure 3 the pressures corresponding to the added air in the gaseous range lie closely on a straight line. Any deviation from this straight line becomes quite evident when condensation begins. The

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[1] The temperatures in degrees Kelvin were obtained from the relation °K = °C + 273.160° and are to be considered accurate to 10.010° K.

observed pressures in the vapor-liquid range lie on a smooth curve with respect to air added. The intersection of the line representing the vapor and the line determined by the first two pressures deviating from the vapor line was taken to be the condensation pressure. The geometrical constructions are given in figure 3. The condensation pressures so obtained are believed to be probably accurate to 5 mm and they are, considering the geometrical construction and over-all results, probably high. The method was checked by measuring the condensation pressure of pure oxygen at 86.45° K (table 4 and fig. 5). The condensation pressure obtained was 503.9 mm Hg and the vapor pressure given by Hoge (refs. 9 and 10) at this temperature is 504.2 mm Hg.

Heats of Vaporization

The vaporization experiments with oxygen and nitrogen are summarized in tables 5 and 6, respectively. To convert the experimental data to heats of vaporization the densities of liquid oxygen given by Baly and Donnan (ref. 11) and Mathias and Onnes (ref. 12) and of liquid nitrogen by Baly and Donnan (ref. 11) and Dewar (ref. 13) were used. The temperature scale of the earlier investigators is believed to differ slightly from that of this work; the difference, however, is not sufficiently large to affect the conversion terms. The derivatives of the vapor pressure with respect to temperature were obtained by tabular differentiation of the vapor pressure of oxygen given by Hoge (refs. 9 and 10) and of nitrogen given in the "NBS-NACA Tables of Thermal Properties of Gases" (ref. 14). The heats of vaporization were converted to the nearest tenth of a degree and averaged. The mean heat of vaporization for each temperature is given in tables 5 and 6. The maximum deviation (0.18 percent) of the heats of vaporization from the mean occurred at 62° K in solid nitrogen in which a lower degree of precision and accuracy is expected because of experimental difficulties. Except at 78° K in nitrogen the deviation from the mean is well under 0.1 percent. The final results are compared in tables 7 and 8 and in figures 6 and 7 with previously published values. Of the previous investigations only the results of Alt (ref. 15) extended over a range of temperature. Alt fitted linear relations to the results of his measurements. The equations are compared in figures 6 and 7.

National Bureau of Standards,
Washington, D. C., August 1, 1952.

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TABLE 1

EQUILIBRIUM MELTING TEMPERATURES OF OXYGEN

[Temperature intercept, 54.370° K;
purity, 99.997 mole percent]

1/F	T, °K
5.72	54.3609
4.39	54.3630
2.05	54.3671
1.49	54.3678
1.20	54.3684

TABLE 2

EQUILIBRIUM MELTING TEMPERATURES OF NITROGEN

[Temperature intercept, 63.180° K;
purity, 100.000 mole percent]

1/F	T, °K
7.40	63.17957
4.15	63.17970
3.44	63.17974
1.81	63.17979
1.38	63.17983
1.17	63.17988

TABLE 3

CONDENSATION PRESSURE OF AIR

Relative amount of air added	Pressure, mm Hg
Temperature, 60.00° K	
0	6.9
1	17.1
1.97	24.6
2.92	29.3
3.86	32.5
4.79	34.4
Temperature, 64.97° K	
0	22.3
1	39.9
1.96	55.3
2.90	67.1
3.82	74.7
4.73	80.4
Temperature, 69.01° K	
4.89	68.5
6.83	92.6
8.69	113.8
10.48	130.7
12.22	142.0
13.94	150.1
15.63	157.3
17.30	162.7
18.95	167.3
Temperature, 69.94° K	
0	69.8
1	135.3
1.97	170.3
2.93	189.2
3.88	200.4
4.82	208.2

TABLE 3.- Concluded

CONDENSATION PRESSURE OF AIR

Relative amount of air added	Pressure, mm Hg
Temperature, 75.00° K	
1.96	169.3
2.89	218.8
3.79	265.1
4.66	307.0
5.51	335.0
6.35	352.3
7.18	366.2
8.00	377.1
Temperature, 80.00° K	
1	428.3
1.95	485.4
2.85	538.5
3.71	588.0
4.54	626.8
5.34	647.1
6.13	663.3
Temperature, 83.00° K	
0	758.1
1	798.7
1.95	836.2
2.86	869.3
3.74	893.4
4.60	907.2
5.44	918.8
Temperature, 85.01° K	
0	1,009.8
1	1,037.0
1.95	1,062.5
2.86	1,083.7
3.74	1,103.7
4.59	1,115.7
5.42	1,124.4
6.24	1,132.7

TABLE 4

CONDENSATION PRESSURE OF OXYGEN AT 86.45° K

Relative amount of oxygen added	Pressure, mm Hg
0	302.1
1	364.8
1.94	424.5
2.84	478.3
3.72	502.3
4.58	504.2
5.45	504.5

TABLE 5

HEATS OF VAPORIZATION OF OXYGEN

T, °K	Q, abs j	M, g	Q/m, abs j g^{-1}	$Tv \frac{dp}{dT}$, abs j g^{-1}	l, abs j g^{-1}	L, abs j $mole^{-1}$
68.4065	489.66	2.1128	231.76	0.05	231.71	7,414.7
68.4122	506.02	2.1807	232.04	.05	231.99	7,423.7
68.4146	993.66	4.2870	231.78	.05	231.73	7,415.4
68.40	--------	------	------	----	------	7,418.2
76.0053	1,124.29	4.9716	226.14	.16	225.98	7,231.4
76.0181	946.57	4.1883	226.00	.16	225.84	7,226.9
76.0241	939.87	4.1599	225.94	.16	225.78	7,225.0
76.00	--------	------	------	----	------	7,228.2
84.1392	882.00	4.0215	219.32	.45	218.87	7,003.8
84.10	--------	------	------	----	------	7,004.9
91.2854	941.63	4.4162	213.22	.93	212.29	6,793.3
91.2870	943.07	4.4261	213.07	.93	212.14	6,788.5
91.30	--------	------	------	----	------	6,790.4

TABLE 6

HEATS OF VAPORIZATION OF NITROGEN

T, ^{o}K	Q, abs j	m, g	Q/m, abs j g^{-1}	$Tv \frac{dp}{dT}$, abs j g^{-1}	l, abs j g^{-1}	L, abs j $mole^{-1}$
62.0018	784.87	3.2376	242.42	0.15	242.27	6,787.4
62.0172	753.17	3.1185	241.52	.15	241.37	6,762.2
62.00	------	------	------	----	------	6,775.0
67.9588	778.72	3.6907	211.00	.35	210.65	5,901.6
67.9620	782.46	3.7100	210.91	.35	210.56	5,899.0
68.00	------	------	------	----	------	5,899.0
73.0913	785.35	3.8208	205.55	.70	204.85	5,739.1
73.0887	741.84	3.6134	205.30	.70	204.60	5,732.1
73.10	------	------	------	----	------	5,735.2
78.0153	692.92	3.4581	200.38	1.23	199.15	5,579.4
78.0147	693.58	3.4714	199.80	1.23	198.57	5,563.1
78.00	------	------	------	----	------	5,571.8

TABLE 7

COMPARISON OF HEAT OF VAPORIZATION OF OXYGEN AT NORMAL BOILING POINT (760 MM HG)

[1 defined cal = 4.1840 abs j; see also fig. 6]

Source	Heat of vaporization, abs j mole^{-1}
Shearer (ref. 16)[a]	[b] 8,170
Estreicher (ref. 17)[c]	[b] 7,740
Dewar (ref. 18)[d]	6,848
Alt (ref. 15)	6,818
Barschall (ref. 19)[e]	6,868
Witt (ref. 20)	6,831
Keesom (ref. 21)	6,792
Eucken (ref. 22)	6,690
Dana (ref. 23)	6,830
Giauque and Johnston (ref. 5)	6,814.9
Frank and Clusius (ref. 24)	6,822.8
Clusius and Konnertz (ref. 25)	6,819.9
This research (interpolated to 90.190° K, refs. 9 and 10)	6,824.8

[a] Pressure: 740 mm Hg = 89.9° K (refs. 9 and 10).
[b] Points not plotted.
[c] Pressure: 735.1 mm Hg = 89.88° K (refs. 9 and 10).
[d] Pressure: 760.9 mm Hg = 90.30° K (refs. 9 and 10).
[e] Pressure: 763 mm Hg = 90.4° K (refs. 9 and 10).

TABLE 8

COMPARISON OF HEAT OF VAPORIZATION OF NITROGEN AT NORMAL BOILING POINT (760 MM HG)

[1 defined cal = 4.1840 abs j; see also fig. 7]

Source	Heat of vaporization, abs j $mole^{-1}$
Shearer (ref. 16)[a]	5,838
Dewar (ref. 18)	5,900
Alt (ref. 15)	5,582
Witt (ref. 20)	5,810
Eucken (ref. 22)	5,703
Dana (ref. 23)	5,593
Giauque and Clayton (ref. 6)	5,576.8
This research (interpolated to 77.395° K, ref. 14)	5,592.2

[a] Pressure: 737 mm Hg = 77.14° K (ref. 14).

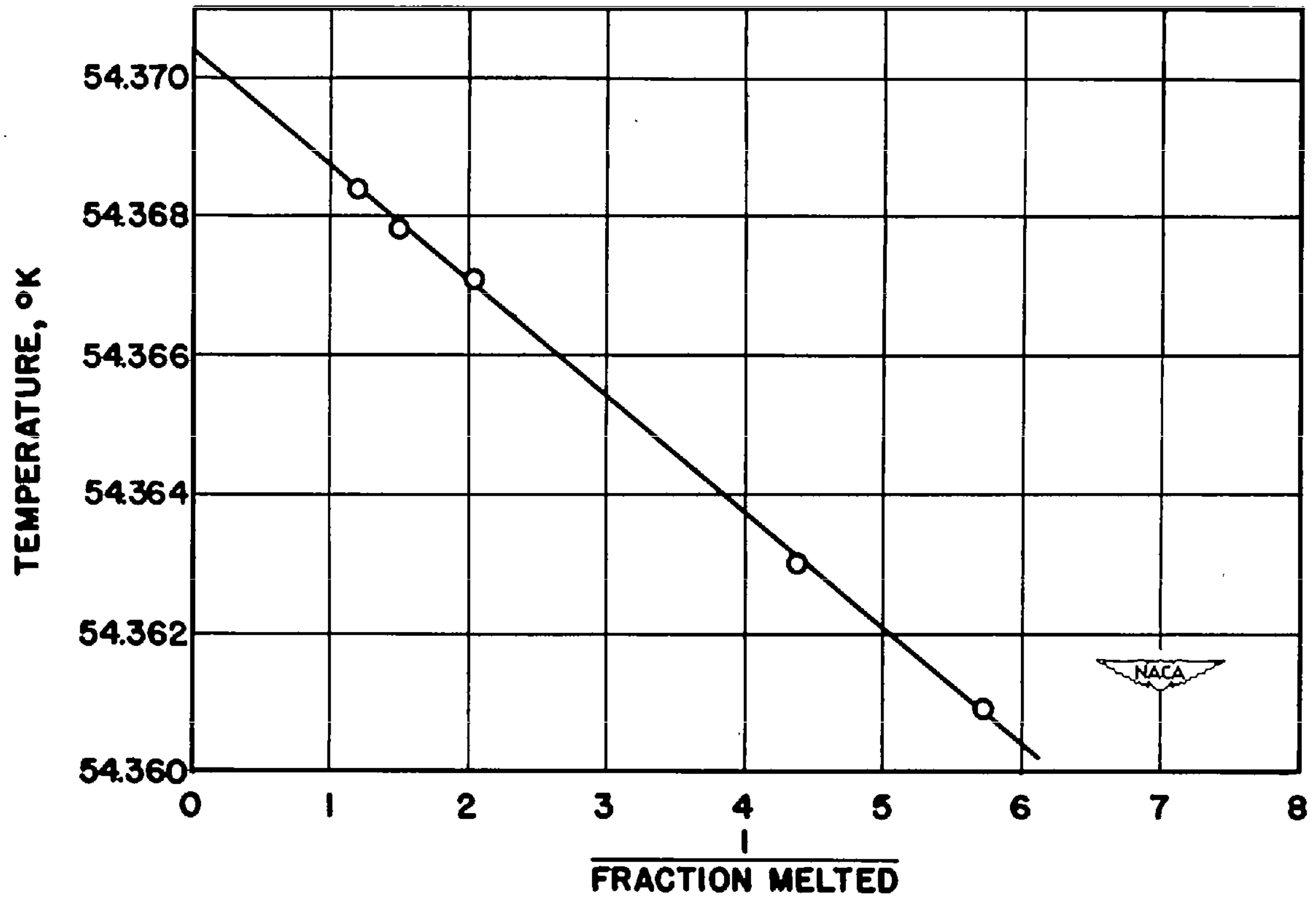


Figure 1.- Melting curve of oxygen sample. Slope, -0.00166; temperature intercept, 54.370° K.

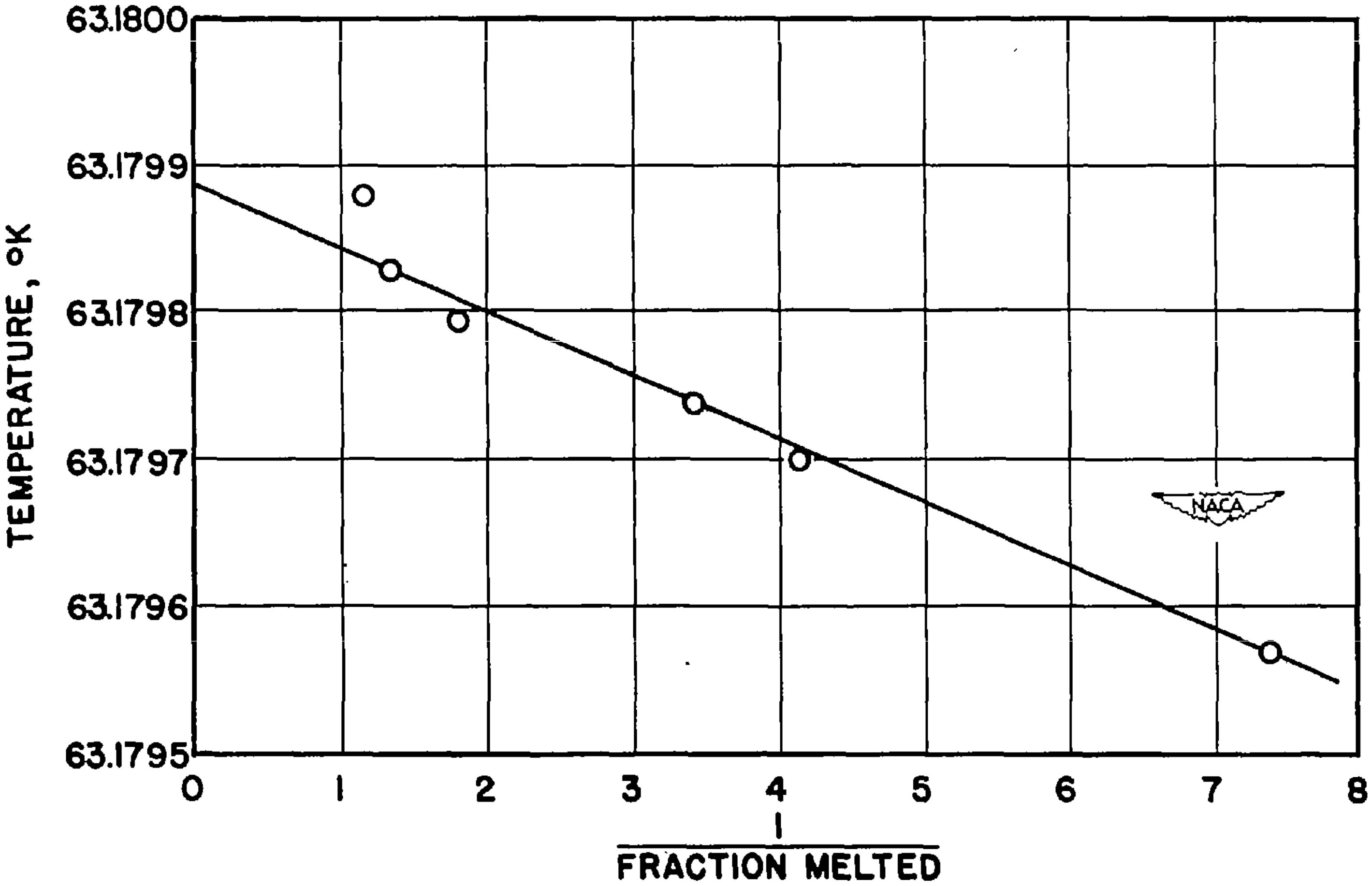
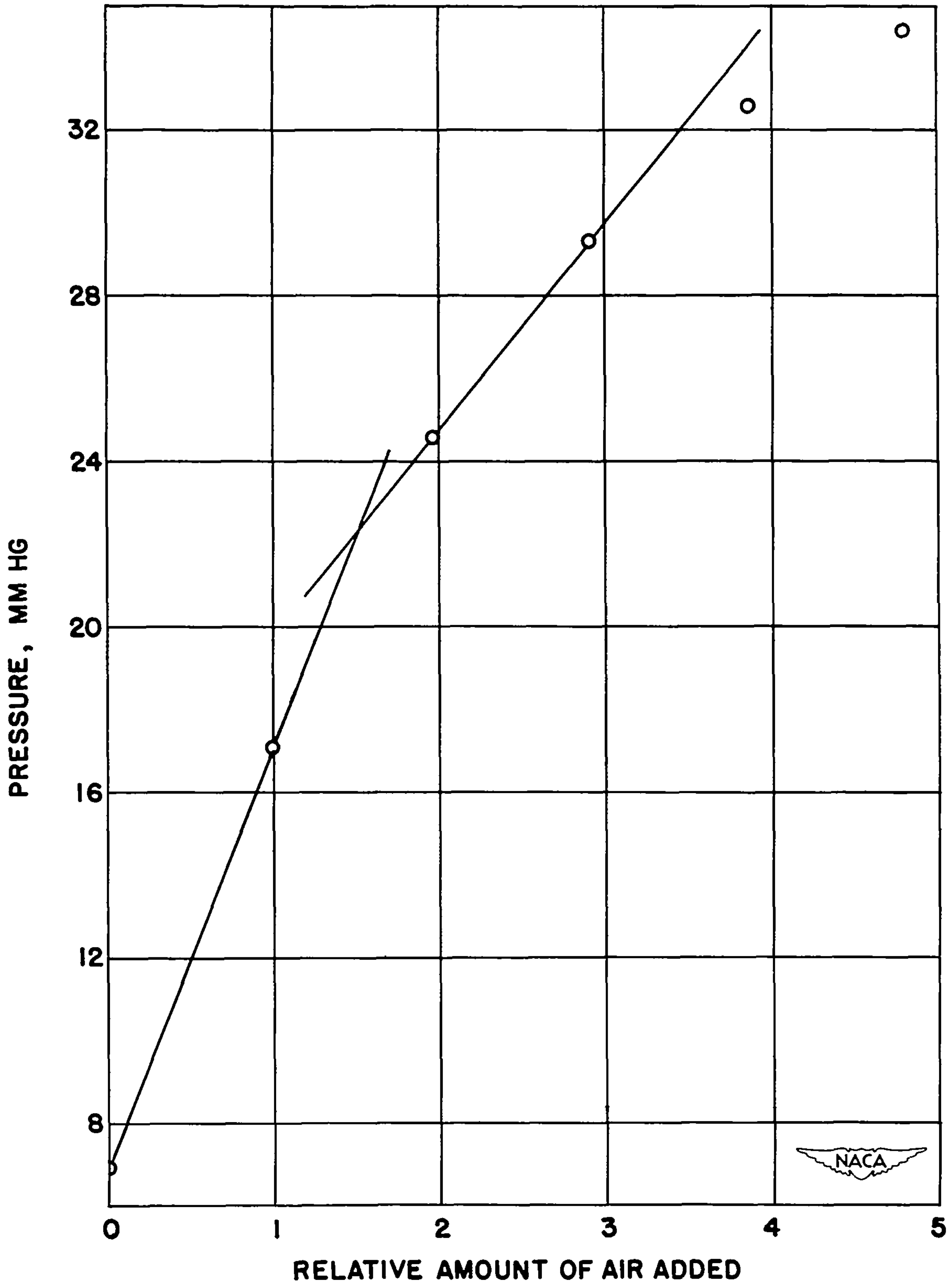
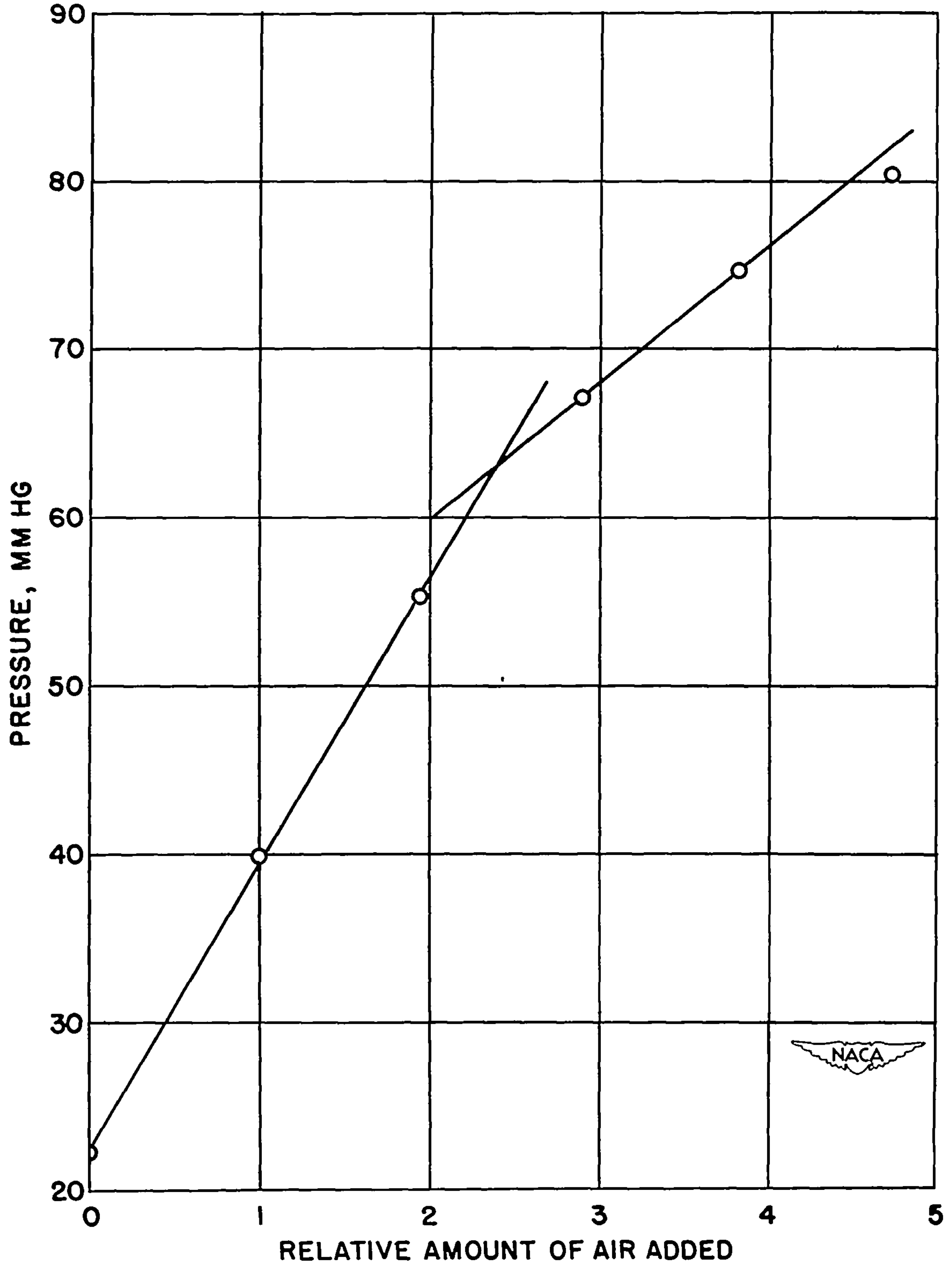


Figure 2.- Melting curve of nitrogen sample. Slope, -0.000043; temperature intercept, 63.1799° K (approximately 63.180° K).



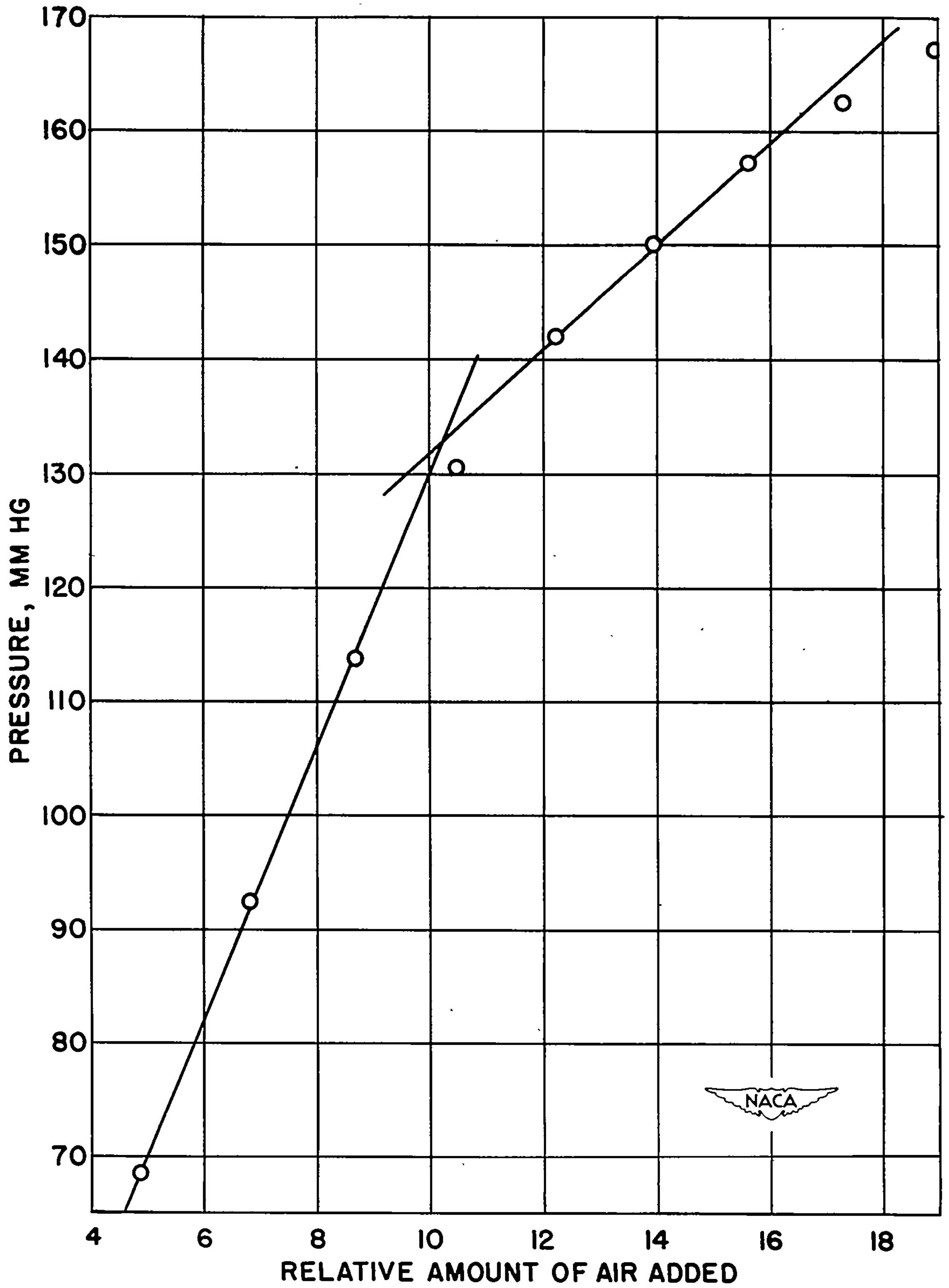
(a) Temperature, 60.00° K; intersection, 22.5 mm Hg.

Figure 3.- Condensation pressure of air.



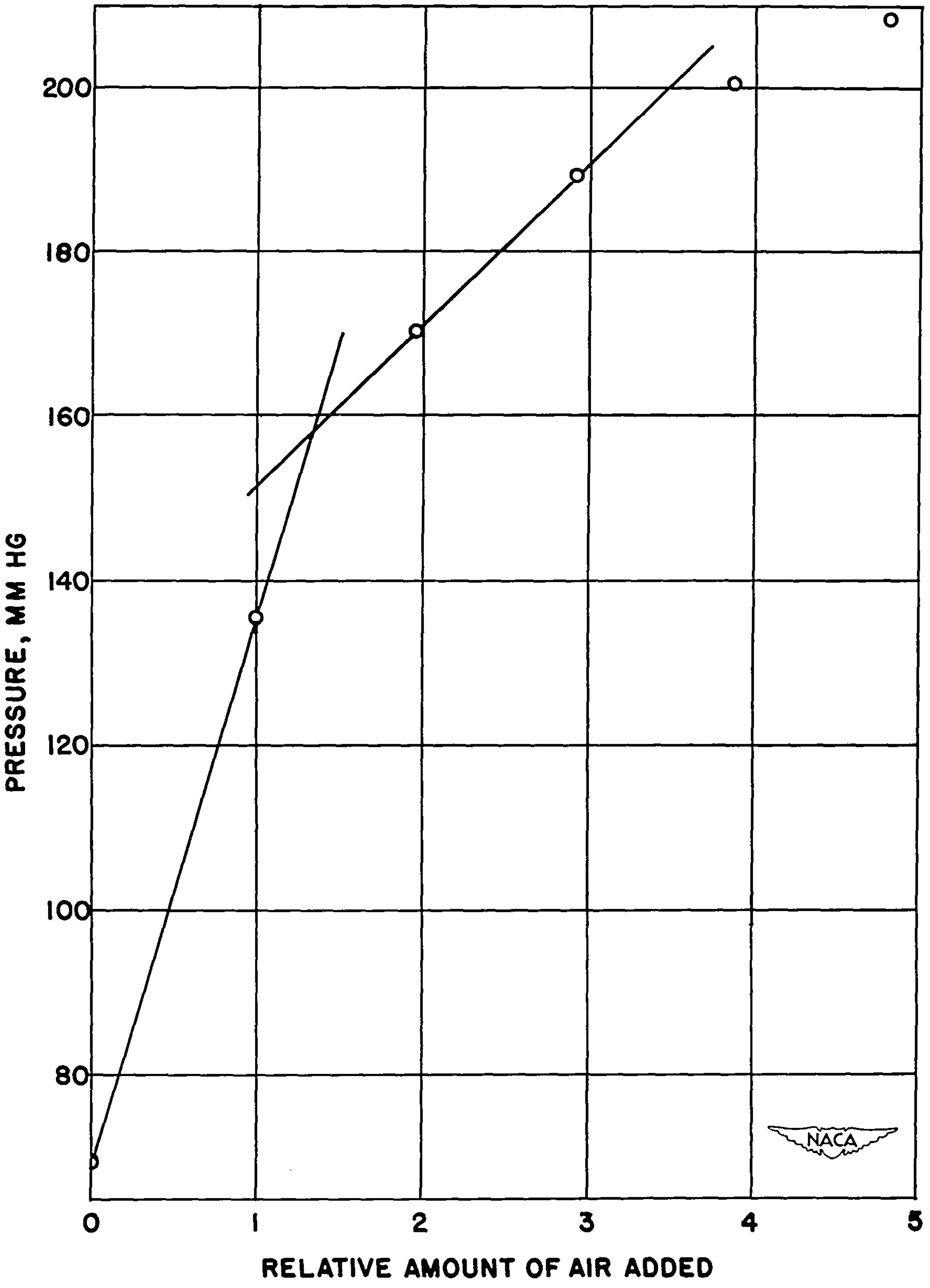
(b) Temperature, 64.97° K; intersection, 63 mm Hg.

Figure 3.- Continued.



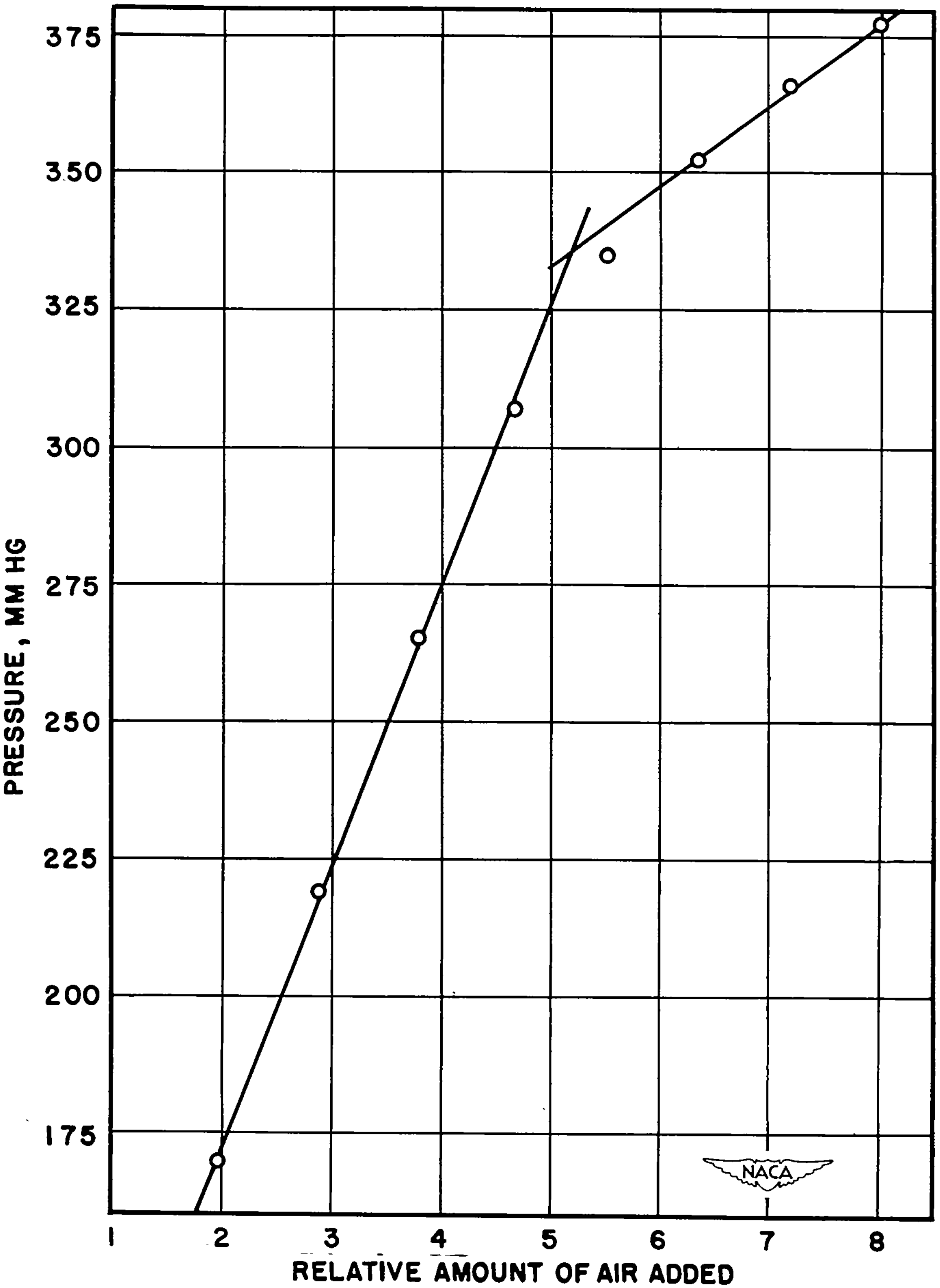
(c) Temperature, 69.01° K; intersection, 133 mm Hg.

Figure 3.- Continued.



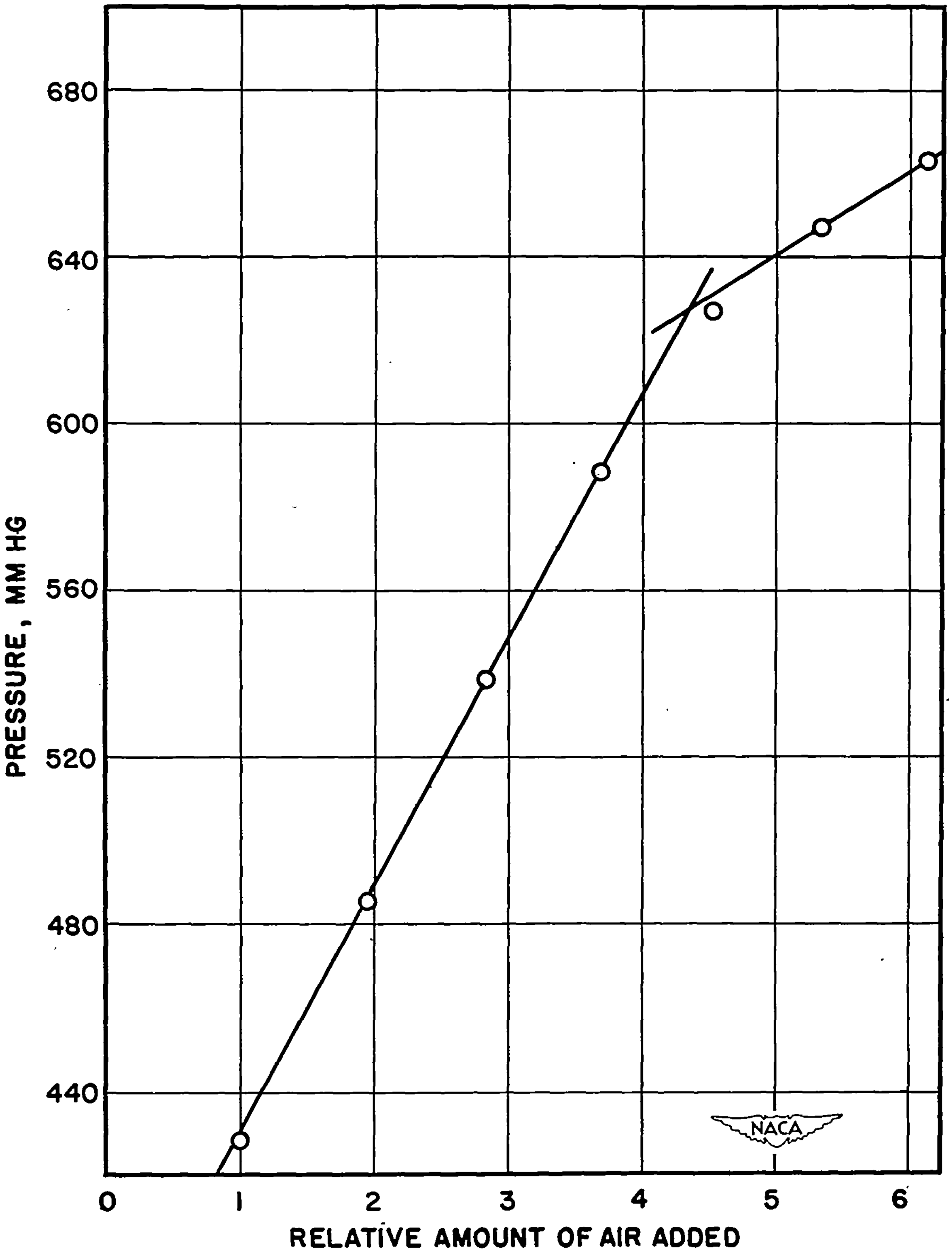
(d) Temperature, 69.94° K; intersection, 158 mm Hg.

Figure 3.- Continued.



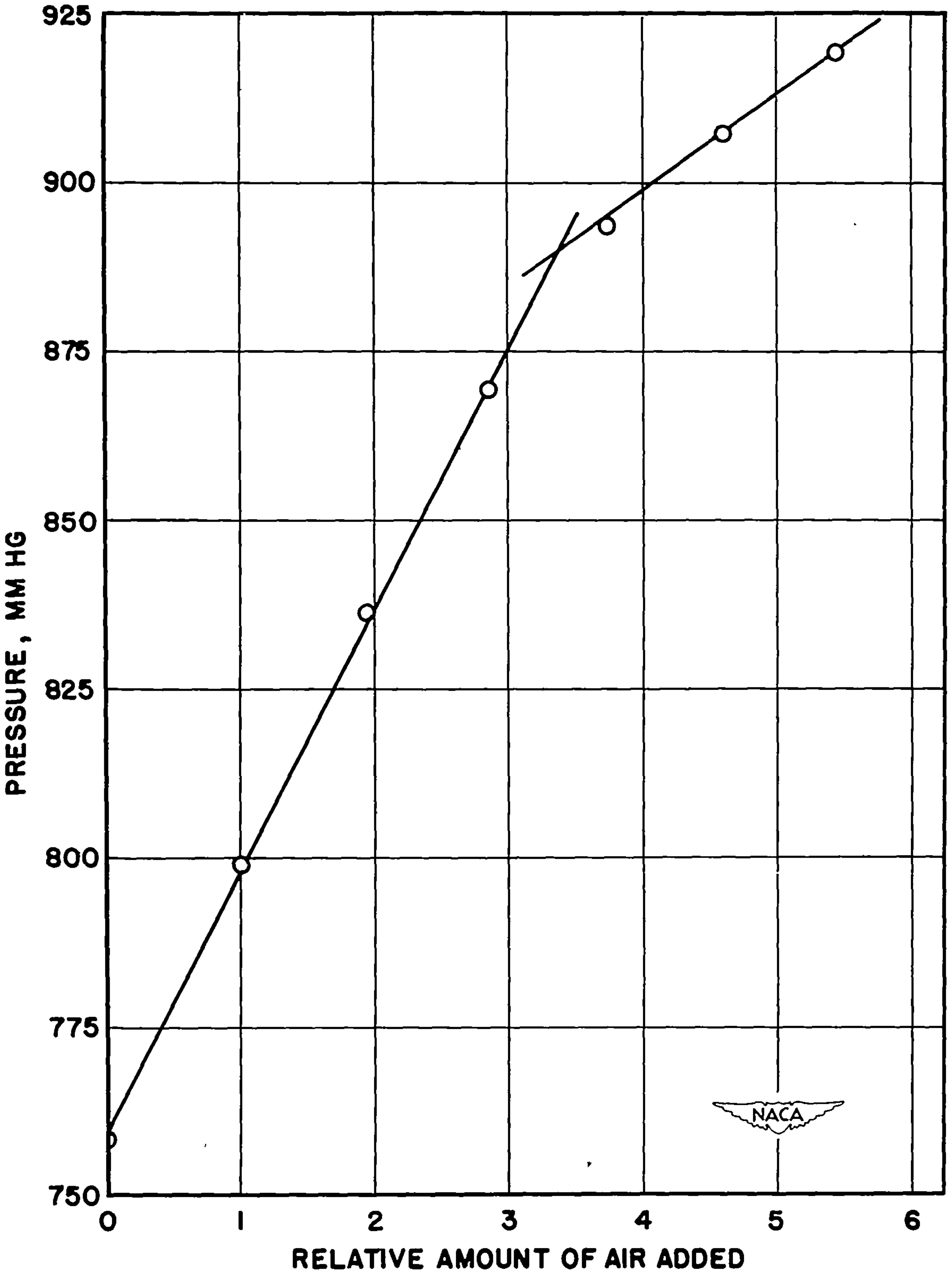
(e) Temperature, 75.00° K; intersection, 335 mm Hg.

Figure 3.- Continued.



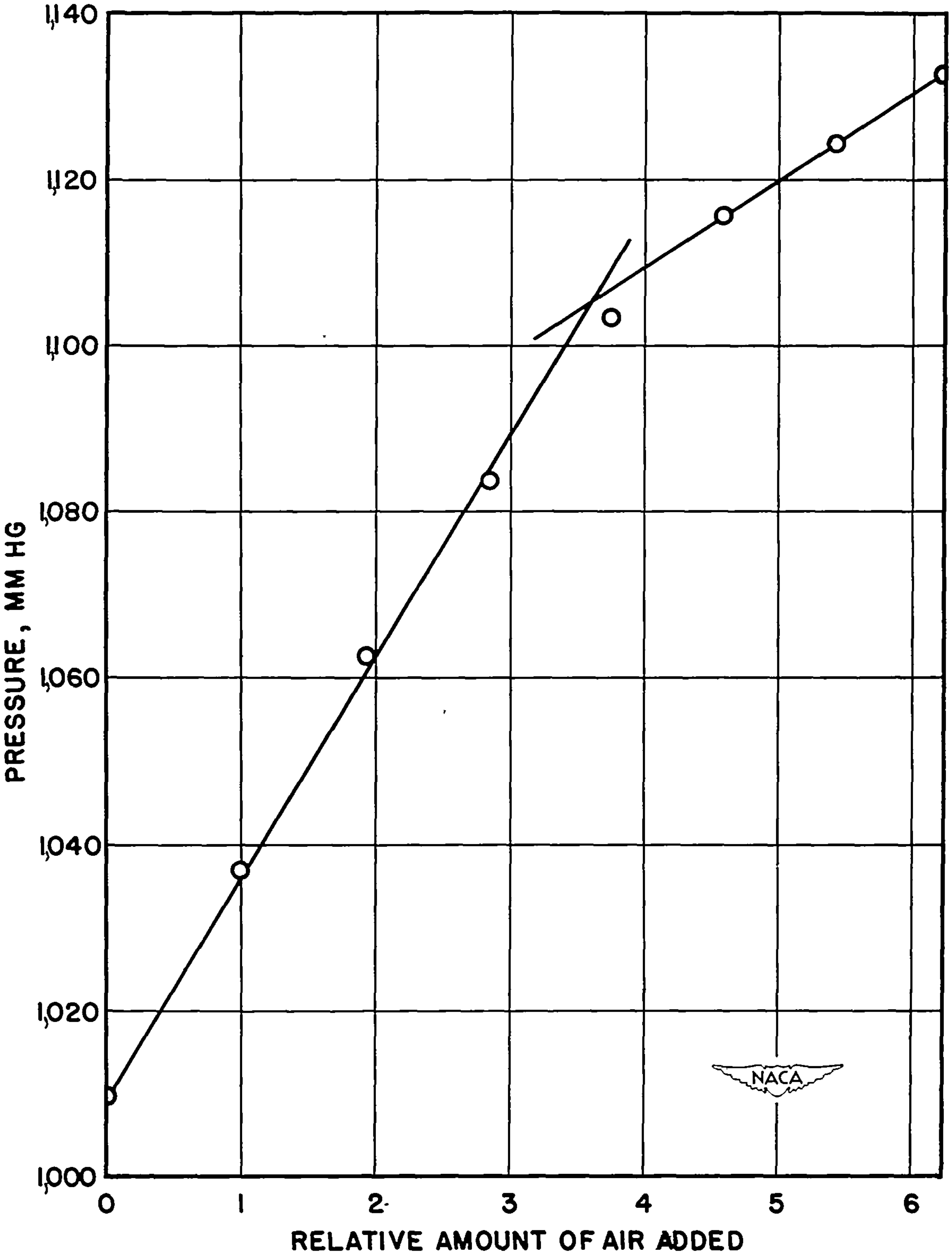
(f) Temperature, 80.00° K; intersection, 628 mm Hg.

Figure 3.- Continued.



(g) Temperature, 83.00° K; intersection, 891 mm Hg.

Figure 3.- Continued.



(h) Temperature, 85.01° K; intersection, 1,105 mm Hg.

Figure 3.- Concluded.

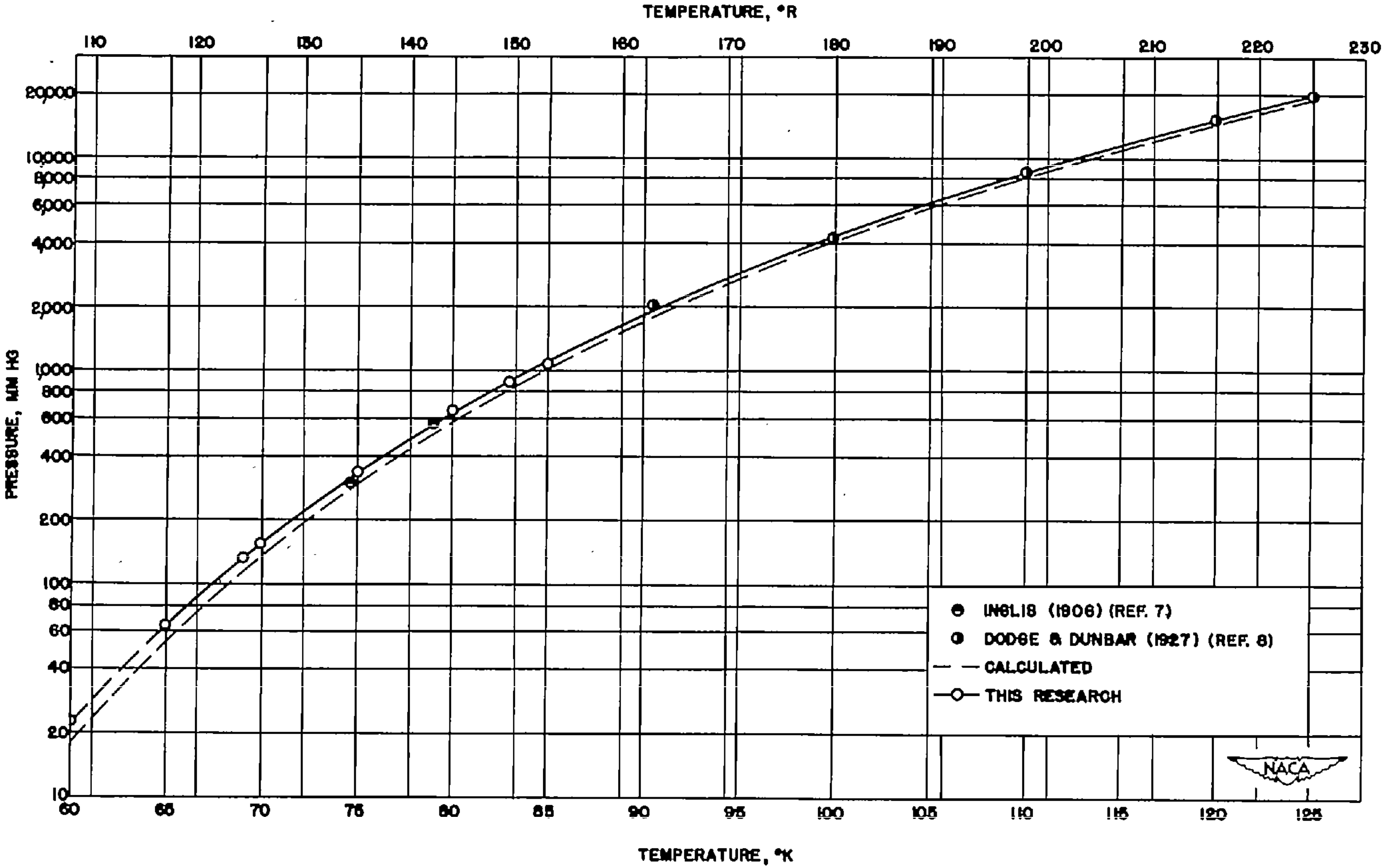


Figure 4.- Condensation line of air.

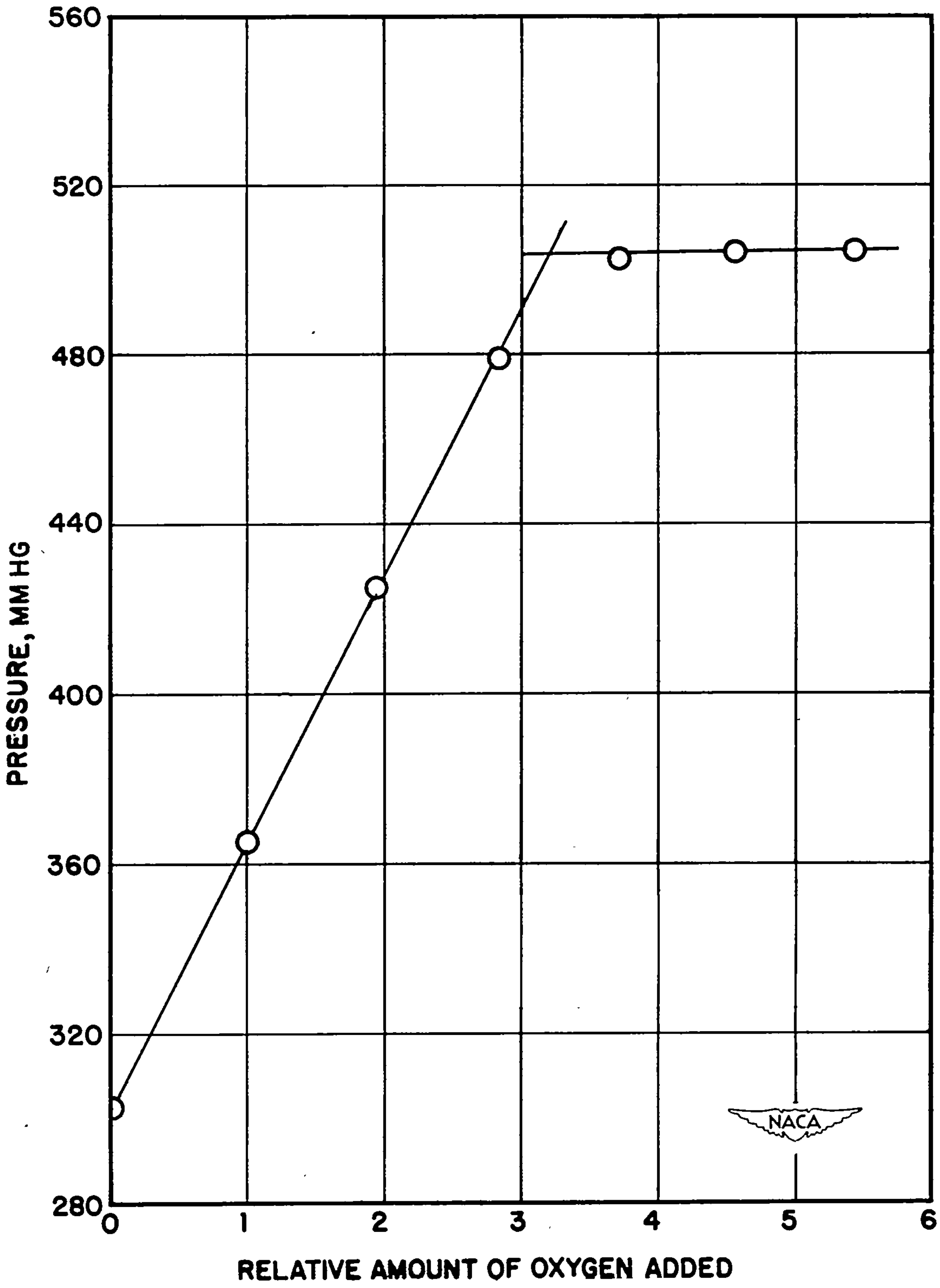


Figure 5.- Condensation pressure of oxygen. Temperature, 86.45° K; intersection, 503.9 mm Hg.

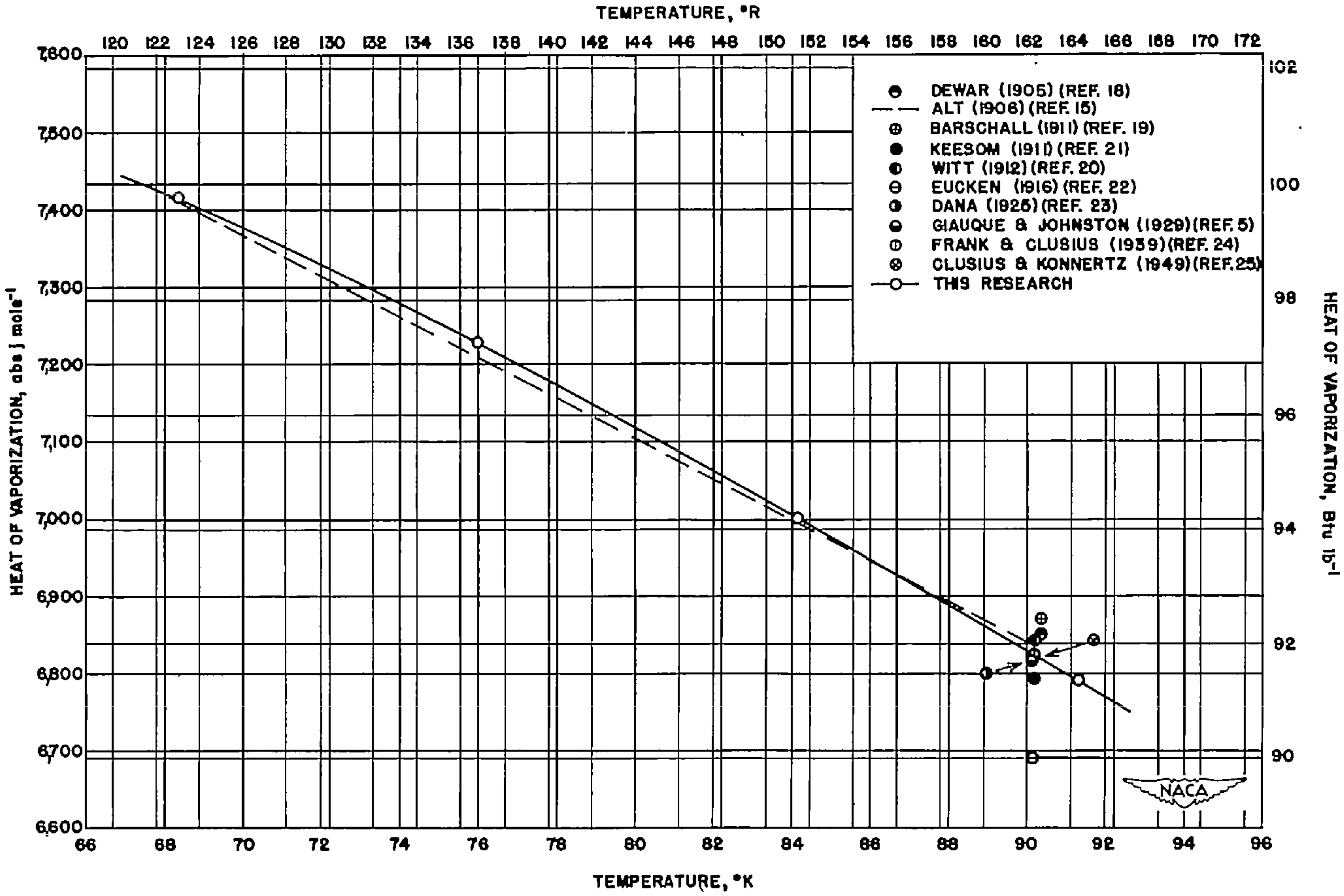


Figure 6. - Heat of vaporization of oxygen.

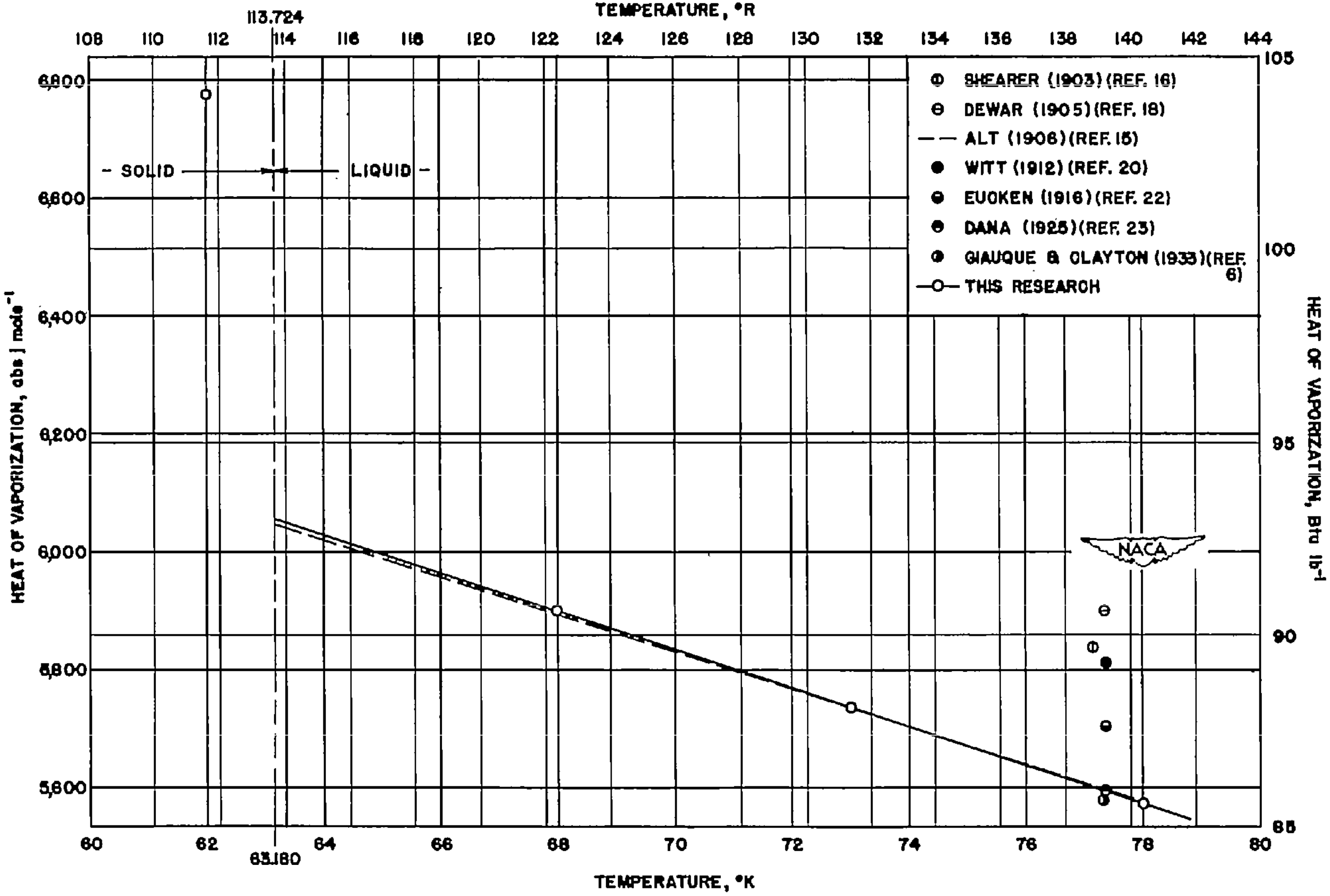


Figure 7.- Heat of vaporization of nitrogen.

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