TABLE V.

Temp. ° C.	Pressure (mm. Hg.). Iso-butane.	Normal butane.	Propylene.
130	...	20600	...
120	21700	18100	...
110	18600	14700	...
100	15400	12500	...
90	13000	10700	...
80	10650	...	27400
70	8700	6700	22800
60	7000	5400	18900
50	5600	4300	15500
40	4400	3350	12600
30	3400	2550	9900
0	...	...	4400

Summary.

The critical data for propylene, normal butane, and iso-butane are given. Vapor pressures of these three gases at temperatures ranging from 0° C. to 130° C. are also shown.

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PITTSBURGH, PA.

[CONTRIBUTION FROM THE LABORATORY FOR GAS RESEARCH OF THE U. S. BUREAU OF MINES.]

THE VAPOR PRESSURES OF SULFUR DIOXIDE AND NITROUS OXIDE AT TEMPERATURES BELOW THEIR NORMAL BOILING POINTS.

BY G. A. BURRELL AND I. W. ROBERTSON.

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In this paper, one of a series, dealing with the vapor pressures of substances at low temperatures, are shown the vapor pressures of sulfur dioxide and nitrous oxide. The method of procedure has been described in previous communications to THIS JOURNAL.[1]

Preparation of Gases.

Sulfur Dioxide.—This was prepared by the action of sulfuric acid on copper. It was bubbled through water to remove sulfur trioxide and finally thoroughly fractionated at the temperature of liquid air to remove atmospheric air or other gases of high vapor pressure at that temperature, and at temperatures between —70° and —100° to remove water vapor and other gases of negligible pressures at those temperatures. Purification was carried to the point where the entire liquid boiled within a range of 0.2°.

Nitrous Oxide (N_2O).—Nitrous oxide was prepared by heating ammo-

[1] THIS JOURNAL, 37, 1893, 1902, 2188, 2193, 2482, 2486 (1915).

nium nitrate. The evolved gases were passed through caustic-potash solution and sulfuric acid and finally thoroughly purified by fractionation at low temperatures. In the vapor-pressure observations, readings were made with a rising and falling mercury column, and checked after boiling away a part of the *liquid gas* in the vapor-pressure bulb.

In Tables I and II are shown the observed and calculated vapor pressures for the two substances, the temperatures given being the average of one reading each on thermometers Nos. 707 and 504. The equations of the curves were calculated from the Nernst formula[1]

$$\text{Log } p = \frac{\lambda}{4.571\text{T}} + 1.75 \log \text{T} - \frac{\epsilon}{4.571} \text{T} + \text{C}.$$

In the case of sulfur dioxide the constants λ, ϵ, and C were found by taking the values of p at the temperatures 262.1°, 248.3° and 208.6° Abs. In the case of nitrous oxide the values of p at 182.5°, 173.6°, and 152.0° Abs. were taken. Above 182.5° Abs. nitrous oxide is liquid and below this temperature it is solid. In this case only the solid phase was considered in calculating pressures.

TABLE I.

Saturated Vapor Pressures of Sulfur Dioxide at Low Temperatures.

Temperature. Average.		Pressure.	
0° C.	Abs.	Obs. Mm. Hg.	Calc. Mm. Hg.
Liquid			
—11.0	262.1	760	760
—11.9	261.2	730	735
—13.0	260.1	700	697
—14.7	258.4	650	647
—16.4	256.7	600	599
—20.3	252.8	500	499
—24.8	248.3	400	400
—30.4	242.7	300	292
—37.8	235.3	200	196
—42.3	230.8	150	149
—48.3	224.8	100	101
—57.5	215.6	50	52
—64.5	208.6	30	30
Solid			
—72.9	200.2	16	15
—76.0	197.1	12	11
—81.3	191.8	7	6.5
—87.4	185.7	3	3.4
—94.4	178.7	0.5	0.2

Equation of curve = Log P = — 1951.46/T + 1.75 log T — 0.01277T + 9.4408

TABLE II.

Saturated Vapor Pressures of Nitrous Oxide at Low Temperatures.

Temperature. Average.		Pressure.	
0° C.	Abs.	Obs. Mm. Hg.	Calc. Mm. Hg.
Liquid			
— 88.7	184.4	760	...
— 89.3	183.8	730	...
— 90.1	183.0	700	...
Solid			
— 90.6	182.5	666	666
— 91.0	182.1	650	646
— 91.9	181.2	600	600
— 93.9	179.2	500	500
— 96.4	176.7	400	399
— 99.5	173.6	300	300
—103.7	169.4	200	200
—106.7	166.4	150	149
—110.8	162.3	100	97
—117.2	155.9	50	48
—121.1	152.0	30	30
—127.0	146.1	15	14.3
—131.3	141.8	7	8.0
—138.9	134.2	4	4.2
—144.1	129.0	1	1.2

Equation of curve = Log P = — 1096.72/T + 1.75 log T + 0.0005T + 4.8665

[1] "Theoretical Chemistry," 1911, p. 719.

In Figs. 1 and 2 are shown the plot of the temperature, 0° C. and ° Abs. against the pressure, mm. of Hg, and the logarithm of the pressure against

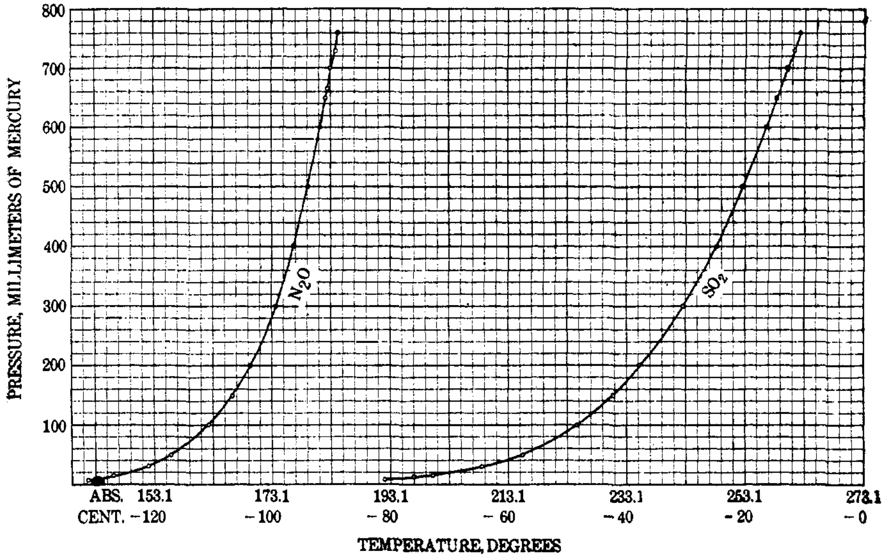

Fig. 1.—Plot of temperature against pressure.

the reciprocal of the absolute temperature. The straight lines shown were drawn by obtaining an equation from the average of all the results

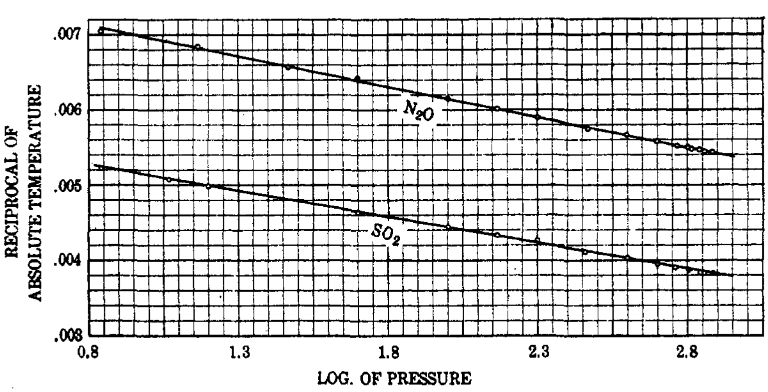

Fig. 2.—Plot of reciprocal of absolute temperature against log. of pressure.

computed by the method of least squares and drawing the lines according to these equations. For liquid sulfur dioxide the equation is

$$\text{Log } P = -1448.01/T + 8.425.$$

For solid nitrous oxide

$$\text{Log } P = -1232.2/T + 9.579.$$

The average heats of evaporation over the temperature range studied (calories per gram-molecules) were calculated from the Clausius-Clapeyron equation

$$Q = (d\, ln\, p)RT^2/dT.$$

By integrating this equation, one obtains

$$ln\, P = -Q/RT + \text{const.}$$

The values 1448.01 and 1232.2 represent the average of all the determined points on the curve. Using these values in the Clausius-Clapeyron equation and changing from common to natural logarithms, one finds in the case of liquid sulfur dioxide: Q = 1448.01 × 4.571 = 6619 calories; for solid nitrous oxide: Q = 1232.2 × 4.571 = 5632 calories.

Saturated vapor pressures of nitrous oxide below the normal boiling point have not been determined by other investigators. For the normal boiling point, Faraday[1] found —87.2°, Cailletet[2] found —92°, and Ramsay and Shields[3] found —89.8°. The agreement is not good. Our value is —88.7°.

Saturated vapor pressures for sulfur dioxide have been determined by Regnault[4] from —30° to 65°, and by Pictet[5] from —30° to 50°. A comparison of their work with that of the authors of this paper follows:

Temperature. °C.	Pressures (mm. Hg.).		
	Regnault.	Pictet.	Burrell and Robertson.
—10	760	760	...
—11	...	...	760
—15	608	578	640
—20	479	464	508
—25	372	418	398
—30	296	274	306

Neither Regnault's nor Pictet's work, when plotted, makes a smooth curve. Some of the points are from 1° to 3° off the curve.

Summary.

Saturated vapor pressures of sulfur dioxide and nitrous oxide are shown. For sulfur dioxide the vapor pressures range from 760 mm. at —11.0° to 0.5 mm. at —94.4°. For nitrous oxide the vapor pressures range from 760 mm. at —88.7° to 1 mm. at —144.1°.

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[1] *Phil. Trans.*, **135**, 1, 155 (1845).
[2] *Arch. de Gen.*, **66**, 16 (1878).
[3] *J. Chem. Soc.*, **63**, 833 (1893).
[4] *Mem. de l'Acad.*, **26**, 535 (1862).
[5] *Arch. de Genève*, **13**, 212 (1885).