

4. The free electrolyte formed in the above platinum sols (as distinguished from that which may be adsorbed and takes relatively little part in the conductivity) corresponds to an electrolyte concentration of 0.0001 to 0.0003 *N*.

5. The presence of chloride, bromide, iodide, or hydroxide ion in concentrations ranging from 0.00005 to 0.005 *N* (approximately) has a marked stabilizing effect on gold sols, and furnishes a quick and reliable method of preparing these sols.

6. The stabilizing effect is not produced by dispersion of the gold in pure water and subsequent addition of the electrolyte.

7. The upper limit of electrolyte concentration for a particular anion seems to be governed somewhat by the precipitating power of the cation.

8. The lower limit of electrolyte concentration required to produce a red sol is, within a wide range, independent of the concentration of colloid formed.

9. The particles in all of these red sols have been shown by electrophoresis to be negatively charged.

10. The stabilizing effect is not observed on the addition of fluoride, nitrate, sulfate, or chlorate ion in similar concentrations.

11. The stabilizing effect seems to be closely related to the ability of the ion to form stable compounds with gold. No gold, however, could be detected in the filtrate obtained after coagulation of the sol. The amount of gold compound necessary to stabilize the colloid is probably extremely minute.

12. Electrical synthesis of colloids is considered to consist of a thermo-mechanical dispersion of the metal which is followed by the formation of a colloidal complex between the dispersed metal and certain ions present in the medium.

In conclusion we desire to express our appreciation of generous assistance and advice from members of this department and of the Department of Physics.

NEW YORK, N. Y.

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

THE CRITICAL CONSTANTS OF NORMAL BUTANE, ISO-BUTANE AND PROPYLENE AND THEIR VAPOR PRESSURES AT TEMPERATURES BETWEEN 0° C. AND 120° C.

By F. M. SEIBERT AND G. A. BURRELL.¹

Received September 27, 1915.

In this report, one of a series dealing with the vapor pressures of gases, are shown the critical constants of *N*-butane, isobutane and propylene

¹ Published by permission of the Director of the Bureau of Mines.

and their vapor pressures at temperatures from 0°C. up to 120°C. These data had not been previously determined. They were needed by this laboratory in work on the liquefaction of gases at different temperatures.

Preparation of Gases.

The physical properties of substances in the neighborhood of their critical points are seriously affected by the presence of minute traces of impurities; hence it is of the utmost importance to obtain as pure material to work with as possible. Therefore, extreme care was exercised in the preparation of the gases selected for the work. Final purification was accomplished in every case by fractionating the gases at low temperatures. In some cases, for instance in separating normal butane, normal boiling point -0.3° , from possible traces of isobutane, normal boiling point¹ -13.4° , fractionation was conducted at a pressure of less than 1 mm. of mercury; hence the process was tedious to carry out by working with a hand-operated vacuum pump, and, therefore, the operation was made automatic, as described later.

Isobutane.—Isobutane was prepared by the reaction between isobutyl iodide and the zinc-copper couple. The evolved gas was collected over caustic potash. Next it was introduced into a bulb surrounded by liquid air, and atmospheric air or other gases of sufficient vapor pressure at the temperature of liquid air were removed by repeated fractionations with a Töpler pump. Fractionation of the gas was repeated until no more gas was given off. Next the gas was fractionated at a temperature of -120° to -115° . At this temperature the vapor pressure of normal butane is practically nil (it is 1 mm. at -99.9°) and the vapor pressure of isobutane is below 1 mm.² This procedure freed the isobutane of any possible traces of normal butane. Fractionating at -120° to -115° was tedious, hence the operation was made automatic by connecting a bulb immersed in liquid air with the bulb containing the liquid gas under examination. As a result the gas distilled over into the liquid-air bulb with but little attention from the operator. After about three-fourths of the liquefied gas had distilled the distillation bulb was sealed off. This process was repeated about 10 times, the whole operation requiring one week's time. Of course, water vapor and other gases whose vapor pressures are entirely negligible at a temperature of -120° to -115° are also removed at the same time. But as further precaution the gas was fractionated several times at a temperature of about -98° . At this temperature the vapor pressure of isobutane is about 7 mm., hence fractionation proceeded faster.

Normal Butane.—This was prepared by the reaction between normal

¹ Lebeau, *Chem. Zentr.*, 1908, II, 292, gives -10.5° and Noyes, *THIS JOURNAL*, 30, 142 (1908) gives -11.5° .

² See *THIS JOURNAL*, 37, 2188 to 2193, 2482 to 2486 (1915).

butyl iodide and the zinc-copper couple. It was collected over caustic potash and purified by fractionation at low temperatures.

Propylene.—Propylene was prepared by dehydrating propyl alcohol with phosphoric anhydride. It was collected over caustic potash and purified by fractionation at low temperatures.

Criteria of Purity.

1. The vapor pressures determined by the authors were independent of the relative volumes of liquid and vapor.
2. The logarithm of the pressure plotted against the reciprocal of the absolute temperature gave a straight line.
3. The critical phenomena were normal and different samples of condensed liquid gave identical results both as to vapor pressure and critical constants.
4. All the vapor in the experimental tube could be condensed to the liquid phase without a perceptible rise of pressure.

The Critical Constants.

Critical Temperature.—Young¹ defines the critical temperature as the temperature at which the volume of saturated vapor and that of the liquid are equal.

When a gas is compressed below its critical temperature the volume of the liquid increases, the vapor decreases and a sharp meniscus is present. As the critical point is approached the meniscus becomes flatter and less distinct; finally a mist or opalescence appears within a small range of temperature. It should make no difference from which side the critical temperature is approached: the same phenomena at the same temperature should be reproduced from either side. The critical point was taken to be that at which no meniscus was visible when the volume was constant, and at which it just appeared when the volume was slightly increased. In the duplicate experiments of the authors the critical temperatures never differed by more than 0.1°.

Critical Pressure.—The critical pressures were determined by means of the compression machine shown in Fig. 1² and read by means of the air manometer when the critical temperature was reached.

Calibration of Manometers.—The air manometers (e) and (d), Fig. 1, consisted of two capillary tubes with white backgrounds, having an internal diameter of about 0.8 mm. and a length of about 500 mm. They were graduated in millimeters and accurately calibrated by filling them with mercury and allowing any desired portion to flow through a small capillary stopcock sealed to the tubes. The volumes were calculated

¹ *Proc. Roy. Dublin Soc.*, 12, 407 (1910).

² Similar in most respects to one used by Sidney Young and constructed at this laboratory by O. P. Hood, chief mechanical engineer and W. F. Hausstein, instrument maker, and F. E. Donath, glassblower.

from the weights of mercury drawn off. After the tubes had been calibrated over their entire length, one end of each was closed and the volume up to a chosen mark which had not been affected by the sealing-off process was obtained by introducing mercury through a very fine hair-like tube,

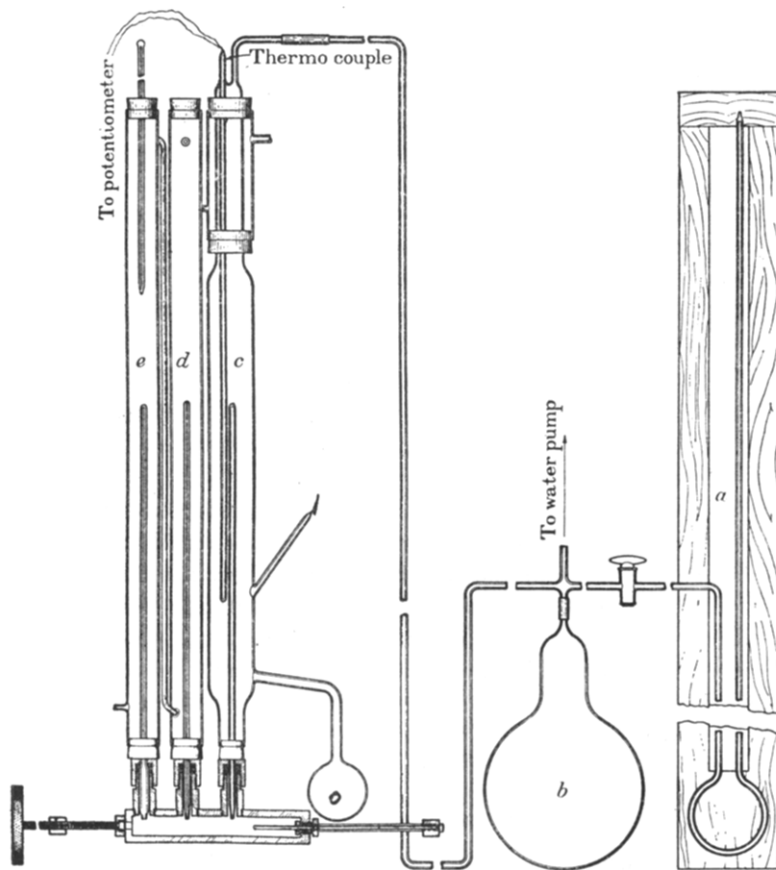


Fig. 1.—Compression apparatus for determining critical data and vapor pressure.

noting the position of the mercury in the tube and then withdrawing it with the same small tube and weighing it. After several check operations the volume of the closed end, with reference to a graduation on the tube, was determined by weighing the mercury drawn off.

One of the tubes served as a high-pressure and the other as a low-pressure manometer. The low-pressure tube was then blown out slightly at the open end so that a small ridge was formed which prevented it from slipping from its rubber cap when introduced into the compression machine.

To the high-pressure tube (*e*), Fig. 1, a small bulb was sealed, so that a much larger mass of air could be introduced. The capacity of this

bulb was about 3 cc. In filling these manometers with air both tubes were sealed to a common train which was in turn sealed to a Töpler pump containing a large tube of phosphoric anhydride. After the tubes had been thoroughly exhausted, dry and CO₂-free air was introduced into them. They were then evacuated, filled with air, again evacuated, etc., nine or ten times, and finally filled at about atmospheric pressure with air which had been passed over phosphoric anhydride and soda lime several hundred times. The ends were then sealed off and scratched with a file so that they could be broken off beneath the mercury in the pump. Next they were fitted into their rubber caps, their ends broken in the reservoir of the compression machine and screwed tightly into the machine.

PV was obtained for the low manometer by fitting into the third opening in the compression machine a long capillary tube, of about 2-mm. diameter, open at both ends, and observing the difference of levels of mercury in the open tube and the low manometer corresponding to several different positions of the mercury in the manometer.

TABLE I.
Barometer = 741 mm.

Low manom. reading. Division number.	Vol. of air at 0° C.	Temp. manometers. ° Abs.	Temp. of open manom. Room temp. ° C.	Diff. of levels corr. to 0°.	Pressure mm. Hg. at 0°.	PV #.
340.0	0.2373	297.7	27.0	107	898	213.1
320.0	0.2365	297.7	27.0	161	902	213.3
300.0	0.2217	297.7	27.0	220	961	213.0
280.0	0.2069	297.7	27.0	289	1030	213.1
260.0	0.1920	297.7	27.0	369	1110	213.1
240.0	0.1774	297.7	27.0	460	1201	213.05
220.0	0.1624	297.7	27.0	569	1310	212.7
201.0	0.1482	297.7	27.0	693	1434	212.5

Mean value of PV = 213.0.

TABLE II.

High-gage reading. Division number.	Vol. of air at 0° C.	Low-gage reading.	Vol. of air at 0°.	Diff. of levels.	Pressure from low gage reading.	PV.	Pressures recalc. from av. PV.
340.0	0.2094	125.5	0.0919	221	2539	531.6	2536
300.0	0.1838	108.0	0.0792	199	2888	530.8	2890
320.0	0.1964	116.9	0.08547	210	2702	530.6	2704
260.0	0.15825	91.9	0.06704	175	3352	530.6	3356
240.0	0.1447	84.0	0.0606	160	3674	531.6	3671
220.0	0.1332	76.5	0.05547	150	3989	531.3	3987
200.0	0.1206	69.1	0.0499	138	4406	531.4	4404
180.0	0.1082	61.9	0.0445	125	4911	531.4	4909
140.0	0.0836	47.9	0.0341	100	6346	530.1	6354
120.0	0.0713	41.0	0.0289	87	7455	531.5	7450
100.0	0.05928	34.5	0.02402	75	8942	530.1	8957
70.0	0.04144	24.7	0.01663	54	12862	533.0	12818

Mean value of PV = 531.2.

Table I gives the data employed in calculating PV for the low-pressure manometer used in this work.

The foregoing set of observations was used to obtain PV for the high-pressure manometer, as follows:

The open tube was removed from the compression machine and a small plug of glass inserted in its place in the cap. The plunger was screwed up until the mercury in the high-pressure gage appeared on the graduations. Readings were then taken on both gages.

The data obtained for the high gage are given in Table II.

The figures in the sixth column of Table II were calculated from

$$P = \left(\frac{\text{PV (for low gage)}}{\text{Observed volume} \times 273/T} + \text{difference of levels in gages} \right).$$

Method of Filling the Tubes with Substances for Investigation.—The tubes (*c*), Fig. 1, to contain the condensed gases were about 500 mm. long and had an internal diameter of about 2.5 mm. One end was sealed up and on the other end a small ridge was blown to prevent it from slipping from the rubber cap in the compression machine. This latter end was then drawn out very thin (in order to facilitate subsequent sealing off) and sealed to a train to which a bulb was also sealed. Pure gas introduced beforehand into a Töpler pump was then condensed in the bulb by means of liquid air and pumping carried on until all traces of air (possibly accidentally introduced) were removed from the gas. Several evaporations and condensations were always made and the pumping continued to be sure that no air was present. Finally some gas was condensed in the experimental tube and then allowed to evaporate. About 1 to 1½ inches of liquid gas was then condensed with liquid air in the tube and all the excess gas pumped off. The tube was then sealed off, scratched with a file, and set in the compression machine. By this method of sealing, alteration of the gas by the flame of the blowpipe did not occur, because at the temperature of liquid air the vapor pressures of the gases are negligible and hence no vapor was present at the point of sealing. Next the piston of the compression machine was driven up until the tip of the tube was broken off beneath the mercury, whereupon the latter rushed into the tube and trapped the liquid gas.

Method of Carrying Out a Determination.—After the tube (*c*) Fig. 1, containing the gas, was screwed tightly in the compression machine, the jacket shown in Fig. 1 was set and some lead oxide mixed with glycerol applied to the stopper supporting the jacket in order to make a tight joint.

Some mercury was poured down the side tube (*h*, Fig. 1) to cover the rubber stopper and the substance (in one experiment chlorobenzene boiling under different pressures) which served for maintaining the desired jacket temperature was introduced into the bulb *o*, through the same

side tube, (*h*, Fig. 1). It was then closed with a plug of glass and a rubber tube. The liquid in the bulb was then boiled by means of a gas flame and the pressure on the vapor therein read by means of a scale (*a*, Fig. 1), and regulated by means of a water pump. The temperature was approximately read from tables given by Travers.¹

The final temperature readings were obtained by means of a potentiometer and a copper-constantan thermocouple calibrated² against a mercury thermometer in turn calibrated by the Bureau of Standards. Temperatures were read to 0.02°. The arrangement is shown in Fig. 1.

When the vapor in the jacket tube was at the required temperature, readings of the vapor pressure were taken with the liquid and vapor occupying different volumes. The best procedure, as has been pointed out by Young,³ was to condense all the vapor by increasing the pressure by means of the piston and then draw out the piston again while ebullition took place. Readings were taken with the vapor occupying a small volume and again when it occupied a larger volume.

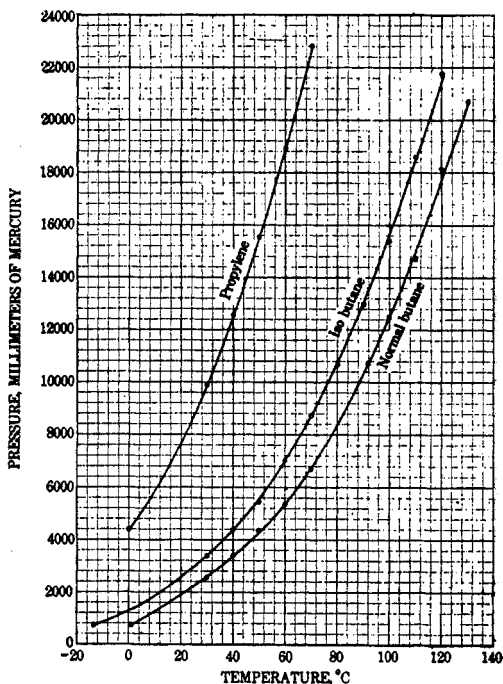


Fig. 2.—Temperature, °C plotted against pressures, mm. of Hg.

TABLE III.
Method of Calculating the Vapor Pressure of Propylene at 50°.

Gage reading.	Temp. of manom. °C.	Vol. of air at 0°.	PV/V at 0°.	Diff. of levels in two tubes.	Amagat's correction.	P.
58.0	24.0	0.03446	15414	+217	—120	15511
58.1	24.0	0.03455	15374	+310	—120	15564

When the vapor and liquid were in equilibrium the machine was tapped with a stout block of wood in order to cause the mercury columns to settle. Next readings were taken from the high-pressure gage. The pressure

¹ "Experimental Study of Gases," 1902, pp. 317, 318.

² Calibrated with the assistance of J. K. Clement, physicist of the Bureau of Mines.

³ *Proc. Roy. Dublin Soc.*, 12, pp. 396 (1910).

was obtained from PV of the high-pressure gage, also from the difference of levels of mercury in the experimental and manometer tubes. A correction was applied for the compressibility of air as determined by Amagat.¹

The authors could check their temperatures within 0.1° and their pressures within 0.5%.

Curves.

The authors have plotted curves of the results of the investigation as follows:

Fig. 2 shows the temperatures plotted against the vapor pressures of normal butane, isobutane and propylene, respectively.

Fig. 3 shows the $\log p$ and $1/T$ plot for the substances used in this investigation and also that used for the measurement of vapor pressures at low temperatures.

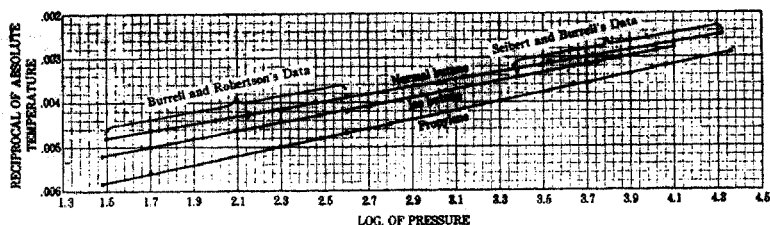


Fig. 3.—Logarithm of the pressure plotted against reciprocal of the absolute temperature.

It will be observed that the vapor pressures as determined by the present authors for normal butane, isobutane, and propylene at temperatures between 0° C. and 130° C. fall on the same straight line as the vapor pressures determined by Burrell and Robertson at low temperatures.²

In Table IV are shown the critical data for the three gases under investigation, also a and b as calculated from van der Waals' equation.

TABLE IV.—CRITICAL DATA.

Substance.	Temp. 0° C.	Press. Mm. Hg.	Press. Atmos.	a .	b .
Normal butane.....	153.2	27113	35.67	0.02883	0.005470
Isobutane.....	133.7	27771	36.54	0.02562	0.005096
Propylene.....	92.6	34463	45.34	0.01668	0.003692

a and b were calculated from van der Waals' equation:

$$a = \frac{27}{64(273)^2} \frac{T_k^2}{p_k} \quad b = \frac{1}{8.273} \frac{T_k}{p_k}$$

In Table V are shown the vapor pressures of the three gases at different temperatures.

¹ Given in Traver's book on "The Experimental Study of Gases," page 234.

² THIS JOURNAL, 37, 1915, 2188 to 2193, 2482 to 2486 (1915).

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.

The authors are indebted to Dr. G. A. Hulett, consulting chemist, and to I. W. Robertson, junior chemist to the Bureau of Mines, for valuable assistance in conducting this work.

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.

Received September 29, 1915.

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).