water cap or submarine, even for a precision of 0.1 per mille, with one proviso. They are inferior to these two for preventing the flow of heat along thermometers, rods or wires.

It is necessary, not only for the highest accuracy but for all adiabatic methods and for all rapid methods of fair precision, to have the calorimeter completely surrounded by surfaces of known temperature; the copper jacket cover offers a very easy way of providing such an inclosure.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

THE CRITICAL CONSTANTS AND VAPOR TENSION OF PHOSGENE[1]

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Only one experimental observation of the critical temperature of phosgene is on record, and this is due to Hackspill and Mathieu,[2] who report a value of 183° from a direct observation. Paternò and Mazzucchelli[3] studied the densities of coexisting phases of phosgene, and by comparison of their density curves with Young's curve for pentane deduced the value 187° for this constant and the value 0.5135 for the critical density. No experimental values for the critical pressure of phosgene are on record. Paternò and Mazzucchelli,[3] using the modified van der Waals' relation, $P_c = {}^8/_3\sqrt{2}\ (R/M)\ T_cD_c$, deduced the value 51.5 atmospheres for the critical pressure. The vapor tension of phosgene has been the subject of two published investigations. Atkinson, Heycock and Pope[4] made measurements over a wide range of temperatures, from the boiling point of oxygen to the boiling point of water. Paternò and Mazzucchelli[3] covered a much smaller range, from —19° to +21°; each of two samples used was made the basis of a series of measurements throughout the temperature range studied, the successive series of measurements being made on the residue from the sample used in the preceding series after distilling off a portion of the liquid; in this way any more volatile impurities were progressively removed, and any less volatile impurities were concentrated in the residue. The effect of distillation on the vapor tension at zero of a sample of technical phosgene (prepared from carbon monoxide and chlorine) has been studied by Germann and Birosel;[5] their findings agree excel-

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[1] Part of the material included in this article is from a thesis submitted by Quimby W. Taylor to the Department of Chemistry of Stanford University in partial fulfilment of the requirements for the degree of Engineer in Chemistry, 1923.

[2] Hackspill and Mathieu, *Bull. soc. chim.*, [4] **25**, 482 (1919).

[3] Paternò and Mazzucchelli, *Gazz. chim. ital.*, **50**, I, 30 (1920).

[4] Atkinson, Heycock and Pope, *J. Chem. Soc.*, **117**, 1410 (1920).

[5] Germann and Birosel, *J. Phys. Chem.*, **29**, 1528 (1925).

lently with those of Paternò and Mazzucchelli, whose phosgene was prepared by the oxidation of carbon tetrachloride, and which might, therefore, be suspected of containing some of this less volatile raw material. As a matter of fact, the phosgene used by Germann and Birosel is known to have contained a small amount of antimony trichloride, since the crude phosgene was passed through a purification train containing powdered antimony to remove free chlorine and no effort was made to remove the trichloride that may have been present. Hence, there seems to be little doubt that the lowest vapor tensions recorded by the two pairs of observers were caused by the presence of less volatile substances. The difference, however, between these values, averaging about 554 mm., and the vapor tension of phosgene at zero, as observed by Atkinson, Heycock and Pope, 568 mm., is much too large to be due to this cause. The phosgene used by the English observers evidently contained more volatile impurities.

It was the object of the present investigation (*a*) to determine the critical pressure of phosgene, (*b*) to redetermine its critical temperature, (*c*) to measure its vapor tension in the neighborhood of its boiling point in order to be able to decide between the conflicting data of the Italian and English observers, (*d*) to measure its vapor tension in the neighborhood of its critical point and, finally, (*e*) to evaluate its critical density, using Paternò and Mazzucchelli's experimental values of the densities of coexisting phases and the experimental critical temperature as the basis of the evaluation. The high-temperature measurements were made in 1923[6] on a single specimen of phosgene, the only one of half a dozen samples that survived the high temperature and pressure to which they had to be subjected. It was hoped that an opportunity might be found to extend the observations to other samples and, if possible, to purer ones, before publication but, as this now seems unlikely, it appears wise to present the results of the investigation as far as they have been obtained.

Method

The apparatus employed in the measurement of the critical pressure was a Cailletet apparatus (300 atmospheres), built by the makers of the original Cailletet apparatus.[7] The details of its use and manipulation were the same as those given by Cardoso and his collaborators,[8] to whom the reader is referred for all details and for illustrations.

The pressure was measured with a gas manometer filled with atmospheric

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[6] Reported at the Milwaukee meeting of the American Chemical Society; see *Science*, **58**, 309 (1923). Due to an unfortunate error the critical pressure was given erroneously as 65 instead of 56 atmospheres.

[7] Cailletet, *Ann. chim. phys.*, [5] **15**, 140 (1878).

[8] Cardoso, *J. chim. phys.*, **10**, 470ff. (1912). Cardoso used a Ramsay-Young compressor instead of a Cailletet pump to compress the gas, but this does not affect the manipulation.

nitrogen.[9] The total volume of the manometer was 68.75 cc., the volume of the upper bulb was 0.755 cc., and the volume of the graduated stem was 0.0039 cc. per mm. The pressure range of the manometer was from 35 to 90 atmospheres. The temperature of the manometer during the measurements was maintained in the neighborhood of 16°, the temperature at which Amagat's measurements of the compressibility were carried out. The usual corrections were made. Values of the pressure for any scale reading were obtained from a curve in which scale readings of the manometer were plotted against the pressures P necessary to compress the original volume V of atmospheric nitrogen contained in the manometer to the volume $(V/P)P'V'$[10] represented by the scale readings at regular intervals.

The heating bath was aniline vapor produced by boiling freshly distilled aniline under controlled pressure. Temperature regulation to 0.1° in the neighborhood of the critical temperature was readily obtained. An Anschütz-type thermometer, 150–200°, graduated in half degrees, and calibrated to tenths by the Bureau of Standards, was mounted directly on the tube containing the phosgene sample.

Measurements of the vapor tension below room temperature were made in an apparatus similar to that used by Germann and McIntyre[11] for measuring the vapor tension of phosgene solutions; a small bulb immersed in a constant-temperature bath contained the liquid and the pressure was measured on a 10mm.-bore mercury manometer in communication with it. The sample of phosgene used left no residue on evaporation (freedom from antimony chloride) and showed a minimum vapor tension

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[9] This gas was prepared according to the directions of Leduc [*Ann. chim. phys.*, [7] **15,** 29 (1898)] by passing dry air free from carbon dioxide over a column of hot reduced copper which had been oxidized over a length of 5 cm. at the outlet end of the tube. According to Leduc, this precaution is necessary to avoid contamination of the gas with hydrogen from decomposition of copper hydride, which forms during reduction of the copper oxide. It is a question in the mind of the writer whether this procedure was justifiable in the present instance, since the object was to produce atmospheric nitrogen having the same compressibility as that used by Amagat in his researches. Amagat appears not to have been troubled by this question and gives no details as to the exact conditions obtaining during the preparation of his nitrogen, conditions which, according to Leduc, determine the proportion of hydrogen in the effluent nitrogen. An alternative would, of course, be the use of dry air free from carbon dioxide instead of nitrogen; but Briner and Cardoso and Keesom (see footnote, Ref. 8, p. 482) have observed the gradual oxidation of mercury while in contact with air under pressure, thus changing the volume and the composition of the air, and making results untrustworthy. A redetermination of the compressibility of atmospheric nitrogen with a gas of known composition would appear to be worth while. However, as far as the present investigation is concerned, the accuracy of the pressure readings is probably much greater than the purity of the phosgene used.

[10] See Amagat, *Ann. chim. phys.*, [6] **29,** 107 (1893), for values of $P'V'$.

[11] Germann and McIntyre, *J. Phys. Chem.*, **29,** 102 (1925).

of 556.5 mm. when successive fractions were distilled, the final small residue showing no change in the vapor tension. The thermometer used to measure the temperature of the thermostat was one belonging to the same set as the one used for the critical temperature, so that recorded temperatures are accurate to 0.1°.

Purification and Purity of Phosgene

The sample of phosgene used was prepared by repeated fractional distillation of technical phosgene, following a preliminary chemical purification. The vapor tension of the sample was 556 mm. and this could not be lowered by further fractionation. A number of the tubes filled were provided with Kuenen's magnetic stirrers, but none of these survived the conditions of the critical point; the only tube that did not blow up was one without provision for stirring the phosgene during the observations.

A test of the monovariance of the sample showed that it was not entirely pure, as the sample could not be entirely liquefied at constant pressure. This may mean, of course, that thermal decomposition at the elevated temperature was rapid enough to make an initially pure specimen impure,[12] but other evidence, presented in the discussion of results, indicates that this factor was of minor importance. The writer's experience with phosgene indicates that published methods for the preparation of pure phosgene are unsatisfactory where a really pure specimen is desired.

Results and Discussion

The first six columns of Table I contain the results of vapor-tension measurements near the critical temperature in the order in which they were taken, the temperatures first rising to the critical point, then diminishing. The third and sixth columns contain the calculated pressures, to be discussed presently. The study of the critical phenomena began at about 170° where the meniscus was normal; as the temperature was raised the meniscus began to flatten out, becoming very flat at 181.1°; at 181.7° the meniscus had apparently disappeared, but its location was still visible because of a slight difference in the index of refraction above and below it. A slight increase in pressure caused even this to disappear, preceded by opalescence; after an interval of time the same faint line showing a difference in densities could be distinguished. At 181.8° and above there was no meniscus, nor any difference in densities, as judged by the refraction of light through the sample. Cooling to 181.6° brought about the reappearance of a well-defined flat meniscus. When 181.7° was approached from either direction, which was done a number of times, the same phenomenon took place as before. Obviously, the critical temperature of this sample was between 181.7° and 181.8°, say 181.75°. This value agrees very well

[12] Ref. 4, p. 1414.

with that obtained by Hackspill and Mathieu, 183°; in view of this we have adopted the rounded value 182° for the critical temperature. The observed critical pressure was 55.3 atmospheres; a study of the graph of $\log p - 1/T$ leads to a value for the critical pressure of about 55.6 atmospheres, based on the observed critical temperature. The rounded value, 56 atmospheres, has been adopted for the vapor-tension calculations.

Table I

Vapor Tension of Phosgene

	Press., atm.			Press., atm.			Press., mm. of Hg	
Temp., °C.	Obs.	Calcd.	Temp., °C.	Obs.	Calcd.	Temp., °C.	Obs.	Calcd.
170.3	48.3	47.26	181.7	55.0	55.72	00.0	556.5	557.2
172.8	48.4	49.02	177.5	52.2	52.48	9.5	814.5	806.3
174.0	49.4	49.89	175.8	51.3	51.22	9.6	815.5	809.3
176.3	51.7	51.59	174.2	49.7	50.04	15.0	994	987.0
177.6	52.5	52.57	172.4	48.7	48.74	18.9	1140	1134
178.6	53.3	53.32	169.8	47.0	46.90	19.7	1169	1166
179.9	54.2	54.33	167.3	44.7	45.18	20.9	1222	1216
180.6	54.5	54.87	164.6	44.0	43.37	21.4	1239	1237
181.1	54.6	55.25	162.4	42.1	41.93	21.4	1240	1237
181.7	55.3	55.72	158.4	40.4	39.40	23.6	1337	1334
182.5	56.4	56.34	154.4	38.4	36.98	26.7	1485	1480
181.7	55.3	55.72	147.6	35.6	33.10	27.9	1540	1540
181.6	55.0	55.64	...	..	...	..	....	....

The last three columns of the table contain the results of measurements and calculations made between 0° and 28°. Comparison of these values with those obtained by Paternò and Mazzucchelli on the one hand, and by Atkinson, Heycock and Pope on the other, indicate that the vapor tensions observed by the latter are considerably too high, while those of the former coincide with the values here reported.

The vapor-tension curve for the interval from 0° to t_c obtained by plotting $1/T$ against $\log p$ on a large scale deviates slightly from a straight line; the experimental points are represented satisfactorily by the equation $\log p_t = 4.4659 - (1207.9/T)(13297/T^2)$, where p is the pressure in atmospheres and T is the absolute temperature. The calculated values of the pressures recorded in the table are based on this equation. With the exception of the three values in the neighborhood of 150°, the agreement of the calculated with the experimental values of the pressure is satisfactory.

What influence the dissociation of the phosgene into carbon monoxide and chlorine may have had on the erratic nature of the observations above 150° is uncertain. According to the experiments of Atkinson, Heycock and Pope[12] the degree of dissociation below 200° is constant and very small; they used active charcoal as a catalyst to produce rapid equilibrium, and all measurements were carried out at or near atmospheric pressure. The experimental conditions in the measurement of the critical temperature were very different from those obtaining during the measurement of the dissociation of phosgene: only glass and mercury were in contact with the sample, and the sample itself was under a pressure of 50 atmospheres. That practically no dissociation took place is evidenced by the facts that the mercury surface was hardly tarnished and that the pressures recorded in approaching the critical temperature were reproduced in receding from it, indicating that the gas was no less pure at the end of the heat treatment than at the beginning.

No new density measurements have been made. But an analysis of the densities of coexisting phases at high temperatures given by Paternò and Mazzucchelli,[3] together with two values at 25° and 0° by one of us,[13] leads to the following equation for the rectilinear diameter of Cailletet and Mathias, $s_t = 0.715 - 0.00107\ t$, where s_t is the mean density of liquid and vapor at any temperature t. Using our value for the critical temperature, 182°, the critical density of phosgene may be evaluated thus: $D_c = 0.520$.

In conclusion, we take pleasure in thanking Major General Amos A. Fries, of the Chemical Warfare Service, for his coöperation in supplying the phosgene used in this research.

Summary

A direct measurement of the critical pressure of phosgene has been made, the critical temperature has been redetermined and the critical density recalculated. Vapor-tension measurements have been made at elevated temperatures, and a series of measurements in the neighborhood of room temperature has verified the measurements of Paternò and Mazzucchelli; based on these measurements, the vapor-tension curve has been traced from zero to the critical temperature. The following critical constants are proposed for phosgene: $T_c = 455°$; $p_c = 56$ atm.; $D_c = 0.52$.

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[13] Germann, *J. Phys. Chem.*, **29**, 140 (1925).