[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

THE COMPRESSIBILITY ISOTHERMS OF CARBON MONOXIDE AT TEMPERATURES FROM –70 TO 200° AND AT PRESSURES TO 1000 ATMOSPHERES

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The advent of commercial processes involving the use of gases under extreme conditions of temperature and pressure has placed carbon monoxide side by side with nitrogen and hydrogen in interest and importance. Carbon monoxide constitutes one-half the volume of pure water gas which is now the principal source of hydrogen used in ammonia synthesis. It is also a primary factor in the catalytic synthesis of methanol and other organic compounds that are rapidly assuming tremendous commercial importance.

Very little reliable information is available regarding the physical properties of compressed carbon monoxide. Natterer[1] in 1855 reported an investigation of the compressibility of this gas at pressures between 77 and 2790 atmospheres. His results are relative to a PV value of 1.000 at 77 atmospheres; the temperature is not stated. Amagat[2] investigated the compressibility of carbon monoxide at pressures from 24.1 to 304.1 atmospheres at temperatures ranging from 18 to 22°. His results are presented in arbitrary units and show only changes in the PV factor with change in pressure. Very recently, Scott[3] has presented data for the 25° isotherm of carbon monoxide at pressures to 170 atmospheres. Botella[4] has determined the isotherms at 0, 12.44 and 20.22° at pressures to 130 atmospheres, and Goig[4a] has collected data at 0° at pressures between 50 and 130 atmospheres. It is apparent that four investigations of the P–V–T relationships of carbon monoxide were proceeding simultaneously and independently. Scott employs a method similar to that used at the Fixed Nitrogen Research Laboratory and at the Physikalische Technische Reichsanstalt of Berlin. Botella and Goig follow in general the method used by Amagat and by the staff of the Cryogenic Laboratory at Leiden. The results obtained in the three investigations are incorporated in our table of results in cases where they cover corresponding ranges of pressure and temperature. In general, our results are from 0.2 to 0.3% higher than those of Scott, Botella or Goig.

It was the purpose of the present investigation to obtain accurate data

[1] Natterer, *Pogg. Ann.*, **94**, 436 (1855).

[2] Amagat, *Ann. chim. phys.*, [5] **19**, 345 (1880).

[3] Scott, *Proc. Roy. Soc.* (London), **125A**, 330 (1929).

[4] Botella, *Anales soc. españ. fís. quím.*, **27**, 315 (1929).

[4a] Goig, *Compt. rend.*, **189**, 246 (1929).

on the compressibility of this gas over a wide enough range of pressure and temperature to meet the present industrial demands. The results also furnish further material for the testing of equations of state for real gases, which are important in theoretical chemistry and in thermodynamic calculations. They also make possible further comparison of the physical properties of carbon monoxide and nitrogen, substances designated as "isosteres," because of their similar electronic structure.[5] The similarity of physical properties of the two gases is very evident at moderate and low pressures even to their temperatures of liquefaction. The new data show the analogy to hold qualitatively at pressures to 1000 atmospheres.

Method.—A quantity of gas at known pressure and temperature is confined in a pipet of known capacity. The gas is allowed to expand into a gas buret maintained at constant temperature and the quantity of gas is determined by measurement of a fixed volume at a measured pressure, not far above or below atmospheric pressure.

Preparation and Purification of the Gas.—Carbon monoxide was prepared in this Laboratory by J. G. Thompson and P. G. Kosting.[6] The method involves the decomposition of formic acid according to the process

$$HCOOH \longrightarrow CO + H_2O \qquad (1)$$

by means of phosphoric acid at 170°. The carbon monoxide was purified from traces of undecomposed acid by sodium hydroxide, then collected in a large steel holder from which it was compressed into steel cylinders to 100 atmospheres. The water in the holder was covered with a layer of heavy mineral oil to retard the diffusion of dissolved air from the water into the gas. Analyses of the carbon monoxide in the steel cylinders by the Orsat method indicated the gas to be free from impurities to within the limits of experimental accuracy. However, later analyses by Kvalnes' low pressure method[7] indicated a possible 0.08–0.10% impurity in the gas from the 100-atmosphere cylinders, while no impurity could be detected in the gas from the gas generator. It is possible that traces of air were introduced during compression.

While it appears possible to produce pure carbon monoxide, impurities are found when it is stored over a period of time in contact with iron. It is believed that the use of copper gas holders, bronze compressors and cylinders and copper lined conduits would have obviated most of the difficulty, but unfortunately such equipment was not available without unjustifiable expense. It was found more expedient to handle the gas quickly and remove the impurities in a purification train under high pressure just before the final measurements were made.

Carbon monoxide is in a metastable condition at moderate and low tem-

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[5] Langmuir, THIS JOURNAL, **41**, 1543 (1919).

[6] Thompson, *Ind. Eng. Chem.*, **21**, 389 (1929).

[7] This method will be described in a separate report.

peratures. It needs but a proper catalyst to bring about the partial decomposition represented by the expression

$$2CO \longleftrightarrow C + CO_2 + 41{,}950 \text{ cal.}^{8} \qquad (2)$$

According to Lewis and Randall the change in free energy (ΔF°) of this reaction at 25° is −29,240 cal. The equilibrium constant (K) may then be calculated from the equation

$$(\Delta F^\circ)_{298} = -RT \ln K \qquad (3)$$

where K is the constant in the expression

$$[CO_2]/[CO]^2 = K \qquad (4)$$

The value of K is found to be 2.65×10^{21}, from which it is calculated that at atmospheric pressure and 25° only $2 \times 10^{-8}\%$ of carbon monoxide is in equilibrium with carbon and carbon dioxide.

High pressure and low temperature favor the formation of carbon dioxide, but low temperature retards the speed with which the reaction takes place. Iron, even in the massive form in which it is present in the gas holder, appears to act as a catalyst for the reaction.[9] Pure carbon monoxide, allowed to stand in the holder exposed to direct sunlight in warm weather for three days, decomposed to such an extent that it could not be used for compressibility measurements without overtaxing the capacity of the purification train. Cylinders of the gas at 100 atmospheres' pressure acquire a carbon dioxide content of over 1% after standing in a protected location for two or three weeks. In addition to this phenomenon carbon monoxide forms with iron, iron carbonyl ($Fe(CO)_5$), a compound that has received much attention recently, first as a source of pure iron[10] and as an anti-detonant[9] in internal combustion engines and, second, as an undesirable impurity in the carbon monoxide gas used in catalytic processes. When this impurity is present large quantities of carbon dioxide appear. The exact mechanism of the reaction is apparently not yet understood. The iron carbonyl itself may be the decomposition catalyst, or the iron carbonyl first formed may decompose, giving catalytically active finely divided iron. The authors are inclined to accept the first explanation. They believe that it more logically accounts for the rapid decomposition of carbon monoxide in the holder and cylinders at room temperature. In order to test this conclusion qualitatively two glass balloon flasks of liter capacity were filled with carbon monoxide. Into one of the flasks was introduced a few drops of a commercial preparation containing iron carbonyl dissolved in a hydrocarbon. After about fifteen days the gases were tested for carbon dioxide. Quantities of carbon dioxide were present in

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[8] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, **1923**, p. 574.

[9] J. H. Frydlender, *Rev. prod. chim.*, **29**, 1 (1926).

[10] I. G. Farbenind A. G., Brit. Patents 269,345, May 10, 1926; 268,770, April 1, 1926; 269,677, Jan. 23, 1926; 281,963, June 25, 1927.

the flask containing the iron carbonyl. The carbon monoxide in the other flask showed no trace of decomposition. No traces of metallic iron appeared in the flask containing the iron carbonyl. Its presence, however, possibly could have been masked by the very evident reddish-brown precipitate that answers to the description of $Fe(CO)_9$.[11] Evidence against our conclusion lies in the fact that carbon dioxide forms rapidly in a steel cylinder at 300°, a temperature which is well above the temperature at which iron carbonyl is stable. It is possible that both iron and iron carbonyl catalyze carbon monoxide decomposition.

Iron carbonyl is an amber colored liquid, with boiling point at 102.5° and freezing point at $-21°$. According to the literature[12] it is decomposed into iron and carbon monoxide at 216°. The authors undertook to remove traces[13] of iron carbonyl from carbon monoxide by means of hot porcelain at about 450°. The result was definite and perhaps to be expected. Carbon dioxide appeared in such quantities as to make its removal practically impossible and the furnace tube shortly became clogged with a mixture of carbon and iron, analyzing in the ratio of about 64 to 1 by weight. More successful were attempts to freeze out the iron carbonyl. For this purpose a deep trap was constructed which was kept continually at a temperature of about $-80°$ by means of a mixture of acetone and carbon dioxide snow. The small diameter intake tube of this trap frequently clogged with solid iron carbonyl. The plug of solid material was removed by applying heat to the tube in conjunction with a large differential pressure.

The carbon monoxide was compressed to high pressure with the same apparatus employed for nitrogen and hydrogen,[14] a description of which appears in earlier reports from this Laboratory. The apparatus from the storage tower of the compression system to and including the high pressure pipet was constructed of bronze.[15] The conduit tubes were copper lined and the hardened valve stems copper plated.

From the high pressure storage cylinder the gas passed through a trap maintained at 0° with ice to remove the bulk of the water vapor, through a tower of crushed fused potassium hydroxide to remove carbon dioxide and

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[11] J. N. Friend, "A Text-Book of Inorganic Chemistry," Vol. IX (II), J. B. Lippincott Co., Philadelphia, **1921**, p. 198.

[12] Bloxam, "Chemistry, Inorganic and Organic," 10th ed., **1913**, p. 456.

[13] Griffith and Holliday [*J. Soc. Chem. Ind.*, **47**, 311T (1928)] found 0.07% of iron carbonyl in carbon monoxide which had been compressed from a steel storage holder, and much less than this in carbon monoxide which had been stored for six months in twenty-year old steel cylinders.

[14] (a) Bartlett, THIS JOURNAL, **49**, 68 (1927); (b) *ibid.*, **49**, 687 (1927); (c) *ibid.*, **49**, 1955 (1927); (d) Bartlett, Cupples and Tremearne, *ibid.*, **50**, 1275 (1928).

[15] The physical properties of this material are discussed in a report from this Laboratory dealing with the compressibility isotherms of nitrogen and hydrogen [THIS JOURNAL, **52**, 1363 (1930)].

more water vapor,[16] through the cold trap at −80° to remove iron carbonyl and traces of water vapor, and finally through a second tower of potassium hydroxide to remove any remaining traces of carbon dioxide. The gas was tested frequently at this point for carbon dioxide by means of a saturated solution of barium hydroxide. It was also tested for iron carbonyl. The presence of even traces of this impurity impart a yellow color to the otherwise brilliant blue carbon monoxide flame. Whenever the tests showed the presence of carbon dioxide the caustic towers were refilled. In general no difficulty was experienced in reducing the iron carbonyl content to a point where it gave but the faintest yellow tinge to the tip of the flame.

TABLE I

THE COMPRESSIBILITY FACTORS, PV, FOR CARBON MONOXIDE

PV = 1 at 1 atm. pressure and 0°

Results marked S are by Scott; results marked B are by Botella; results marked by G are by Goig

Atm.	−70°	−50°	−25°	0°	25°	50°	100°	150°	200°
0	0.7441	0.8173	0.9089	1.0004	1.0920	1.1837	1.3668	1.5498	1.7329
1	.7427	.8162	.9082	1.0000	1.0918	1.1836	1.3671	1.5504	1.7336
25	.7030	.7903	.8938	0.9894	1.0866	1.1822	1.3752	1.5696	1.7577
	....	....	....	....	S1.0835	....	....	....	....
50	.6636	.7622	.8768	.9796	1.0831	1.1826	1.3837	1.5823	1.7758
	....	....	....	G .9763	S1.0797	....	....	....	....
	....	....	....	B .9766	B1.0807	....	....	....	....
75	.6323	.7388	.8632	.9740	1.0832	1.1882	1.3946	1.5977	1.7948
	....	....	....	G .9708	S1.0797	....	....	....	....
	....	....	....	B .9713	B1.0815	....	....	....	....
100	.6147	.7264	.8592	.9745	1.0864	1.1955	1.4062	1.6151	1.8146
	....	....	....	G .9704	S1.0836	....	....	....	....
	....	....	....	B .9705	B1.0852	....	....	....	....
125	.6108	.7247	.8598	.9797	1.0950	1.2069	1.4220	1.6316	1.8357
	....	....	....	B .9751	S1.0927	....	....	....	....
	....	....	....	G .9751	....	....	....	....	....
150	.6190	.7304	.8663	.9889	1.1085	1.2192	1.4388	1.6537	1.8598
	....	....	....	....	S1.1050	....	....	....	....
200	.6631	.7656	.9022	1.0200	1.1415	1.2561	1.4794	1.6987	1.9090
300	.7955	.8872	1.0087	1.1211	1.2406	1.3521	1.5798	1.8054	2.0183
400	.9434	1.0285	1.1403	1.2487	1.3625	1.4716	1.6963	1.9178	2.1380
500	1.0920	1.1755	1.2831	1.3843	1.4940	1.6023	1.8235	2.0450	2.2627
600	1.2386	1.3225	1.4282	1.5256	1.6317	1.7378	1.9557	2.1757	2.3923
800	1.5236	1.6100	1.7153	1.8064	1.9915	2.0144	2.2244	2.4442	2.6602
1000	1.7992	1.8871	1.9935	2.0827	2.1857	2.2879	2.4935	2.7142	2.9264

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[16] Judging from the deep coloration on the caustic at the intake end of this tower, it appears that there must be also some iron carbonyl decomposition at this point.

Experimental Results

The pressure–volume–temperature relationships are expressed in Amagat units. The unit gas mass is that mass of gas occupying 1 liter at 0° and at a pressure of 1 atmosphere. PV is therefore equal to unity under these conditions. The PV values at 1 atmosphere at other than 0° are calculated from the known temperature–volume coefficient of carbon monoxide.[17] All other values given in Table I are unsmoothed experimental results involving no interpolations or extrapolations with the exception of a few data at 100 and 200°, where due to a thermometer correction interpolations were made over a maximum range of 0.3°. The methods of applying these data to pressure–volume–temperature problems in laboratory or plant are presented in an earlier report.[14d]

Temperature and Deviation from the Laws of the Ideal Gas.—The deviation of a gas from the law of the ideal gas is conveniently expressed in the form of a ratio $(PV)/(P_0V_1)_T$ in which $(PV)_T$ is the pressure–volume product at T degrees, referred to unity at 0° temperature and 1 atmosphere pressure, while $(P_0V_1)_T$ is the pressure–volume product at zero pressure at the temperature T. The values of $(P_0V_1)_T$ may be found as the first item in each column of Table I. The results for carbon monoxide are shown in Fig. 1. In order to avoid confusion on the diagram, the experimental points on the curves are not shown. However, every item in Table I has been used in calculating these points and the curves shown pass through every plotted point. The original diagram was of such size that the error in plotting could not exceed 0.1 to 0.2%, while the maximum error of observation is believed not to exceed 0.2 to 0.3%.

Discussion of Results

It is apparent from a study of the curves for carbon monoxide in Fig. 1 and a similar family of curves for nitrogen[15] that the two gases exhibit very similar compressibility phenomena. Carbon monoxide is slightly more compressible in the low pressure range and slightly less compressible in the high pressure range. This is to be expected from the fact that carbon monoxide has a slightly higher critical temperature (−139.0°) than nitrogen (−147.1°). In general, the difference in compressibility becomes less with increasing temperature. These experimental facts are well illustrated in Fig. 2, in which the deviations from the ideal gas law for the two gases at a number of pressures are plotted against temperature. Results for hydrogen are included on the chart to emphasize further the similarity of carbon monoxide and nitrogen.

In a report now published[15] it is pointed out that in the temperature range −70 to 100° and at a pressure of 380 atmospheres, nitrogen exhibits

[17] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, **1928**, Vol. III, p. 16.

approximately a constant deviation from the law of the ideal gas. At this pressure, therefore, and in this temperature range, PV, and hence V, is a linear function of the absolute temperature, a major criterion in the definition of an ideal gas. The family of curves in Fig. 1 shows that carbon monoxide exhibits a similar phenomenon at a pressure of 375 atmospheres and through even a wider range of temperature, −70 to 200°. It can be predicted with certainty that at higher temperatures the deviation curves will "fan out" toward the perfect gas isotherm in a manner similar to curves for nitrogen and hydrogen. In order to establish whether the unique point phenomenon exhibited by nitrogen and carbon monoxide is characteristic of other gases, the available PV data for carbon dioxide, ethylene and oxygen[18] have been investigated. The phenomenon in the case of these gases is not sufficiently evident to justify the statement that it exists.

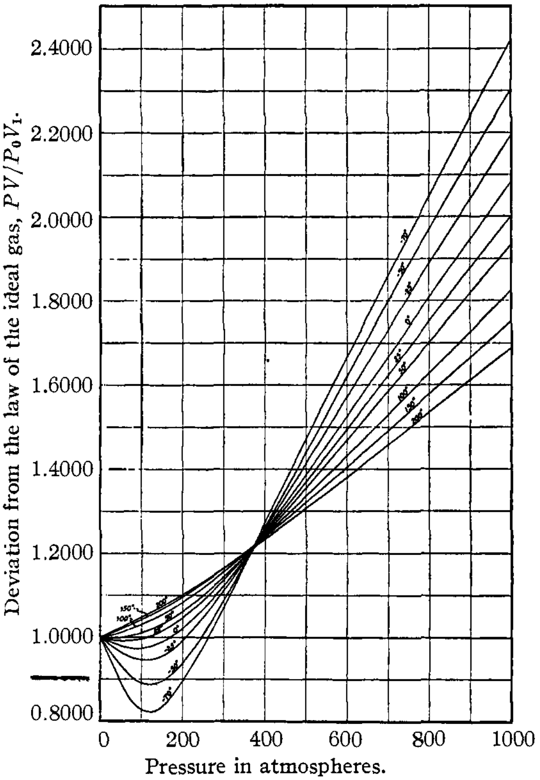

Fig. 1.—Pressure and pressure–volume product of carbon monoxide, $(PV/P_0V_1)_T$.

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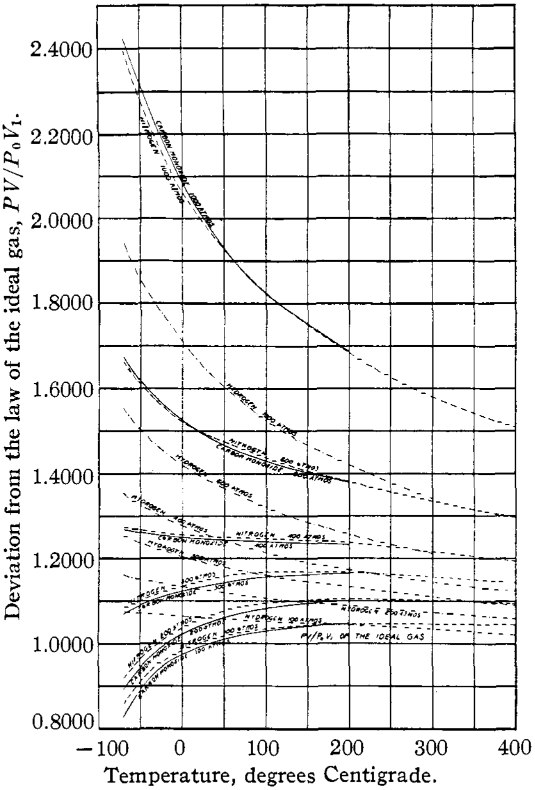
[18] "International Critical Tables," McGraw-Hill Book Co., Inc., New York **1928**, Vol. III, p. 3 *et seq.*

The authors are indebted to the staff of the Fixed Nitrogen Research Laboratory for suggestions and for coöperation in the solving of the many problems met with in this investigation.



Hydrogen, — - — -; nitrogen, — — — —; carbon monoxide, ———.

Fig. 2.—Temperature and deviations from the law of the ideal gas.

Summary

This report has presented the compressibility factors of carbon monoxide at temperatures from −70 to 200° and at pressures to 1000 atmospheres. The results show carbon monoxide to be similar to nitrogen in physical properties at high pressure. In the low pressure range, carbon monoxide is slightly more compressible than nitrogen, while in the high pressure range it is slightly less compressible. At about 375 atmospheres' pressure the deviation of carbon monoxide from the law of the ideal gas is approximately constant (1.217) through the 270° range of temperature. At this pressure

the volume of a given gas mass of carbon monoxide is a linear function of the absolute temperature.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

THE CONSTANTS OF THE BEATTIE–BRIDGEMAN EQUATION OF STATE WITH BARTLETT'S P–V–T DATA ON NITROGEN

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In connection with recent work in high pressure on gases it has been deemed advisable to test some of the recently proposed equations of state. Bartlett has extended his P–V–T measurements on nitrogen and several other gases to include -25, -50, and $-70°$ up to 1000 atmospheres pressure. At pressures below 100 atmospheres data were obtained by Bartlett at this laboratory only sufficient to check the work of other investigators in this low pressure range. The low pressures in Table III were compiled from data furnished by the Reichsanstalt, the Leiden laboratory, and the Massachusetts Institute of Technology. With this complete set of data an equation of state can now be tested throughout a wider range of pressure, volume, and temperature than has hitherto been possible. The Beattie–Bridgeman[1] equation of state was chosen because its propounders have indicated that it reproduces the trends and measurements very well, and because its utility is great, once the constants have been determined, due to its relatively simple algebraic form.

In this discussion P denotes pressures in atmospheres, v denotes specific volumes in cc. per g., and r, the gas constant in cc. atm. per g. per degree. The gas that Bartlett used for these measurements contained 0.07% argon and 99.93% nitrogen. The presence of the argon makes the value of r slightly different from that for pure nitrogen, but ought to have no discernible effect on any of the other constants in the equation of state. The value of r for this gas is 2.92861 cc. atm. per g. per degree.

Since Bartlett's data[2] are listed in the form of isotherms, they were first converted into isochores, by Andrews' method,[3] because this form is better adapted to the determination of the constants in an equation

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[1] Beattie and Bridgeman, *Proc. Am. Acad. Arts Sci.*, **63**, 229 (1928); THIS JOURNAL, **49**, 1665 (1927); and later papers.

[2] Bartlett, Cupples, and Tremearne, *ibid.*, **50**, 1275 (1928). Bartlett and his collaborators have since interpolated these data to even temperatures, and their observations have been extended to include -70, -50, -25, and $20°$. These are published in the preceding article.

[3] Andrews, *Phil. Trans. Roy. Soc.*, **166**, 421 (1876). This method is clearly explained by O. C. Bridgeman, THIS JOURNAL, **49**, 1130 (1927).